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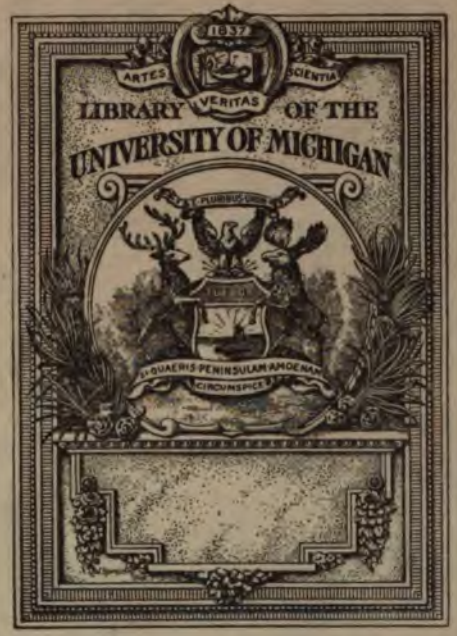
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PAPERS FROM THE CHEMICAL LABORATORIES

No. 70: AN IMPROVED FORM OF APPARATUS FOR THE RAPID ESTIMATION OF SULPHATES AND SALTS OF BARIUM, BY W. R. LANG AND T. B. ALLEN

(REPRINTED FROM THE JOURNAL OF THE CHEMICAL SOCIETY OF LONDON, VOL. XCI.)

No. 71: A BENZENE MODEL ON ONE PLANE FOR LECTURE PURPOSES, BY W. R. LANG

(REPRINTED FROM THE JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, VOL. XXIX.)

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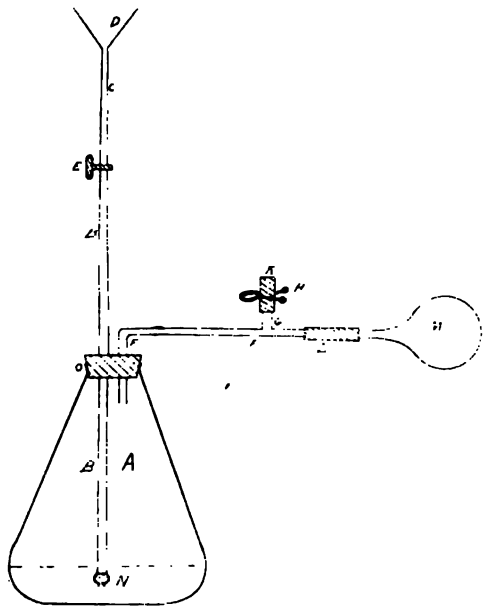
CXXVII.—*An Improved Form of Apparatus for the Rapid Estimation of Sulphates and Salts of Barium.*

By William Robert Lang and Thos. Boles Allen.

N. Tarugi and G. Bianchi (*Gazzetta*, 1906, **36**, i, 347) describe an apparatus for the rapid and exact estimation of sulphates and salts of barium by a volumetric method based on the rapid clearing of turbid solutions in narrow tubes. (For a short description of their apparatus



see Abstr., 1906, **90**, ii, 627.) The authors have modified this apparatus materially; the following short description and diagram will serve to explain it.

The vessel, *A*, containing the acidified sulphate is placed on a flat burner, the approximate amount of barium chloride solution, ascertained by previous rough experiments, run directly into the flask, the stopper, *O*, with its attachments, inserted, and the contents kept at the boiling point. *FF* is a T-tube, on the branch, *G*, of which is fixed a small piece of rubber tubing with a pinchcock, at this stage of the experiment left open to the air. *N* is a small thistle-shaped tube filled with glass-wool which is found materially to clear the turbid solution as it passes up to the narrow tube. The pinchcock, *H*, is then

284686

TABLE IV.

	No. of c.c. of sucrose taken.	Equal to gram sucrose.	Dilution in c.c.	Time of heating in minutes.	No. of c.c. of solution used.	Equal to gram sucrose.	Error in per cent.
(1)	10·00	0·2278	200	5	45·50	0·2275	0·2
(2)	10·00	0·2278	150	5	45·65	0·2283	0·3
(3)	5·00	0·1136	100	5	22·75	0·1138	0·2
(4)	10·00	0·2278	150	5	45·64	0·2282	0·2
(5)	10·01	0·2280	150	5	45·58	0·2279	0·1
(6)	10·00	0·2278	175	5	45·62	0·2281	0·1
(7)	10·00	0·2278	150	8	45·65	0·2283	0·3
(8)	2·00	0·0456	200	5	9·02	0·0451	1·0
(9)	5·00	0·1136	450	5	22·90	0·1145	1·0
(10)	10·00	0·2278	450	5	45·92	0·2296	0·9
(11)	10·00	0·2278	150	15	45·82	0·2292	1·0
(12)	5·00	0·1136	100	20	23·20	0·1160	2·0

These results are some of a number of determinations, and they show that, if suitable conditions are obtained. the results give excellent agreement with the theoretical. The conditions are, first, that the Fehling's solution should be added to the boiling liquid to within 1 c.c. of the correct amount, this being obtained by previous rough titrations; secondly, that the strength of the sucrose in the flask should not be more than 0·15 gram in from 75—100 c.c. of water, and thirdly, that the time of heating should not be more than from five to eight minutes.

CHEMICAL LABORATORY,
UNIVERSITY OF TORONTO.

R. CLAY AND SONS, LTD., BREAD ST. HILL, E.C., AND BUNGAY, SUFFOLK.

A Benzene Model on One Plane for Lecture Purposes.

W. R. Lang.

[REPRINTED FROM THE JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
VOL. XXIX, NO. 6, JUNE, 1907.]

A Benzene Model, on One Plane, for Lecture Purposes.—This model is intended as an aid to teachers in explaining the theory of the constitution of benzene. Any theory regarding its constitution must account for and explain the behavior of benzene towards reagents and its power of forming derivatives. In the aliphatic series it is usual to represent the hydrocarbons graphically with the carbon and hydrogen atoms arranged as in an open chain. The model held as in Fig. 1 would thus represent benzene, showing eight unsatisfied affinities.

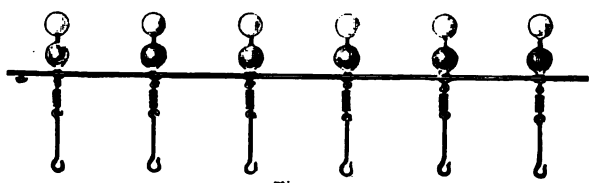


Fig. 1.

But the following summarized characteristics of this body cannot be reconciled with such an open-chain representation, namely :

(*a*) That each of its hydrogen atoms bears the same relation to the molecule, as is evident by the non-existence of isomeric mono-substitution compounds.

(*b*) The formation of benzene as a constant product of the decomposition of the other members of the aromatic series.

(*c*) The formation of hexa-additive compounds (and no more) and the ready breaking up of these into a tri-substitution product.

(*d*) The formation of three di-substitution products.

(*e*) The evident "saturated" nature of benzene.

It is clear from (*c*) that there can be only six unsatisfied affinities, so, if the model is bent round to form a circle, as in Fig. 2, thus linking the first carbon atom to the last, the number of unsatisfied affinities is shown as being reduced to six, and, in addition, each carbon and hydrogen atom is represented as bearing the same relation to the molecule, all being similarly linked.

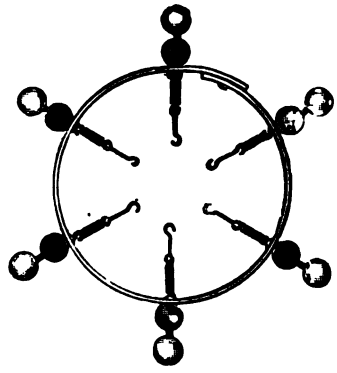


FIG. 2

But the fourth valence of the carbon atoms still appears as unoccupied; these may be represented as acting *towards* the centre—as in the Armstrong-Baeyer formula, or the diagonally opposite atoms may be linked together (Claus); figure 3. If this is done, the model will then represent an exceedingly stable molecule.

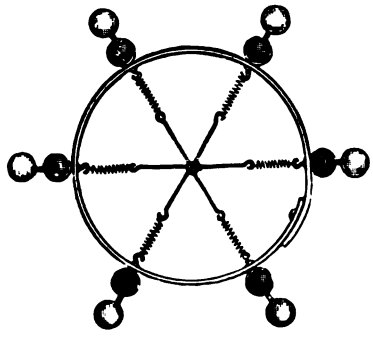


FIG. 3

Small spiral springs are used in the interior of the "ring," to permit of the rapid and secure fastening together of the diagonally opposite

linkings in the last position. The model can readily be constructed from a flexible brass band 1–2 cms. wide, with stiff wires soldered through holes in the rim, while corks of different colors serve admirably for the carbon and hydrogen atoms. It is, however, obtainable from Messrs. Baird and Tatlock, London, E. C.

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No. 72: THE EFFECT OF ACETONE ON THE TRANSPORT NUMBERS OF SODIUM AND POTASSIUM CHLORIDES IN AQUEOUS SOLUTION, BY HENRY F. LEWIS

(REPRINTED FROM THE JOURNAL OF PHYSICAL CHEMISTRY, VOL. XI.)

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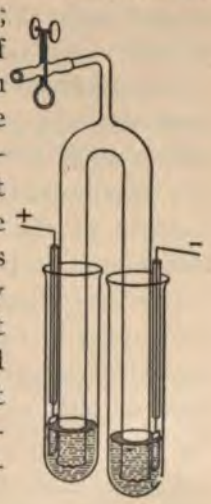
THE EFFECT OF ACETONE ON THE TRANSPORT NUMBERS OF SODIUM AND POTASSIUM CHLORIDES IN AQUEOUS SOLUTION

BY HENRY F. LEWIS

The migration of a number of salts has been studied in solutions in alcohol, glycerine, methyl alcohol, etc., and in every case the transport number was found to be within a few percent of that in pure water. Salts dissolved in mixtures of alcohol and water have also been studied from this point of view with the same result.[1] The following experiments which show that the ratio u/v for the ions of potassium chloride and sodium chloride in aqueous solution is more than halved by addition of acetone are therefore of considerable interest, and must be taken into account in all attempts to interpret the electrical conductivities of these solutions.

The Apparatus

The apparatus with which I worked is not adapted to give results of a very high order of accuracy; as will be seen from the table the results of individual experiments differed by as much as 4 units in the second decimal place. The accuracy was, however, sufficient for the purpose in view, which was to make sure that the transport number is really affected by the presence of acetone; and as the apparatus is easily put together, and determinations may be made with it rapidly, I have thought it worthy of being described, and have detailed a number of test experiments made with it which show that the results of my measurements were not affected by errors due to diffusion or mixing.



[1] An index to the literature of migration determinations in solvents other than water is contained in J. W. McBain's. "Experimental data of the quantitative determinations of electrolytic migration." Trans. Wash. Ac. Sci., 9, 1 (1907).

About 200 cc of solution were used in each experiment. The U-tube was filled by suction, and the pinch-cock closed; the electrodes were then inserted, and connected with a silver voltameter and the source of current. In one experiment a Weston millammeter was used as well as the voltameter; readings were made at one minute intervals during the hour and a half that the electrolysis lasted, and the number of coulombs so obtained agreed within 0.5 percent with that given by the voltameter.

When the electrolysis was at an end, about 12 cc were withdrawn for analysis from the tube *m* ("middle portion"). The pinch-cock on *m* was then slightly opened, and the liquid in the U-tube allowed to run slowly into the electrode tubes, the U-tube being raised so that it never dipped deeply into the liquids in the electrode tubes; the cathode was removed and rinsed into the cathode tube with a little unelectrolyzed solution; these solutions were then removed, cooled, and analyzed.

Thus the anode and cathode portions were easily separated without the use of diaphragms or taps; the legs of the U-tube were rinsed out with the unaltered middle portion of the electrolyte; a middle portion was readily obtained for analysis, and gas bubbles or changes in density at the electrodes could not produce harmful stirring.

The following experiments were made to test the reliability of the apparatus; a decinormal solution of sodium chloride in 50 percent acetone was used.

1. *Diffusion of Alkali from the Cathode.*—A little litmus was added to the solution and turned pink by a trace of acid. After electrolyzing for an hour and a half the blue zone at the cathode extended less than a centimeter into the upright tube.

2. *Diffusion of Acid from the Anode.*—Methyl orange and a little alkali added to the electrolyte gave a yellow solution which after a quarter of an hour was quite red at the anode. In another hour the solution in the anode glass

was bleached, the red remained in the upright tube about a centimeter above the liquid in the glass.

3. *Diffusion of Chlorine.*—Indigo added to the electrolyte was bleached at the anode, but at the end of an hour and a quarter the bleaching had not extended appreciably into the upright tube.

4. *Evaporation of Acetone from the Electrode Glasses.*—A tube was set up in the usual manner, but no electricity was passed through. A Bunsen burner was set near the apparatus so that it might be as warm as during an electrolysis. After two hours the liquid was removed from one side, made up to 100 cc, and analyzed in the usual way; 93.18 cc of the silver solution were required instead of 92.74 cc.

The Method of Analysis

Fifty cc of the unelectrolyzed solution, or 10 cc of the middle portion, were evaporated to dryness on the waterbath to remove acetone; the residue was dissolved in water, 1 cc of a neutral solution of potassium chromate added, and the chlorine determined by decinormal silver nitrate. The cathode solution after electrolysis was made up to 100 cc with unelectrolyzed solution and evaporated as before; the alkali was then neutralized with decinormal sulphuric acid, using methyl orange as indicator, and before titrating with silver a drop of decinormal alkali was added to restore the yellow color. Blank analyses showed that the method was reliable.

The chlorides and the acetone were C. P. preparations of Merck; all measuring vessels and burettes were calibrated.

Results of the Measurements

All the solutions experimented with were approximately decinormal with respect to the salt. The first column of the table gives the parts by volume of acetone in one of the solution. The second, the weight of silver (W) deposited in the voltameter. The third, the duration of the electrolysis in minutes. The fourth, the amount of decinormal silver nitrate required to precipitate the chlorine in 100 cc of the unelectro-

TABLE I

Salt	Parts of acetone	Grams of silver W	Time. Minutes	Analyses		Difference L	Change in middle	H
				Before	After			
NaCl	0	0.1875	45	90.94	79.66	10.28	—	0.59
	⅛	0.1662	60	89.08	80.66	8.42	0.00	0.55
					80.48	8.60	0.05	
	¼	0.1342	60	95.20	89.08	6.12	0.02	0.52
					88.35	6.85	—0.03	
	½	0.1006	65	93.32	89.69	3.63	—0.04	0.38
					89.89	3.43	0.02	
	¾	0.0622	60	89.68	87.43	2.25	0.04	0.38
					87.52	2.16	0.08	
KCl	0	0.1586	40	98.02	90.91	7.11	0.14	0.49
					90.64	7.38	0.09	
	0	0.1928	60	95.12	86.52	8.60	0.12	0.48
	0	0.1232	45	95.12	89.43	5.69	0.03	0.49
	0	0.2020	55	93.31	84.28	9.03	0.18	0.48
	⅛	0.1942	60	96.78	88.94	7.84	0.10	0.44
	¼	0.1844	65	93.20	86.93	6.27	0.00	0.37
					86.69	6.51	0.03	
	¼	0.2020	55	101.14	93.22	7.92	—0.17	0.42
	½	0.1154	60	99.90	95.65	4.25	0.03	0.39
					95.87	4.03	0.05	
	½	0.1232	45	96.22	92.22	4.00	0.02	0.35
	¾	0.0832	75	96.70	94.01	2.69	0.02	0.32
					94.38	2.32	—0.03	
	¾	0.0768	60	100.16	97.98	2.18	—0.04	0.29
					98.24	1.92	—0.03	

lyzed solution; and the fifth, the silver required by the 100 cc of solution obtained by adding unelectrolyzed solution to the cathode solution as explained on page 571. Column six gives the difference between the last two, that is, the loss (L) of chlorine from the cathode compartment. The seventh column gives the loss or gain in the 10 cc middle portion, expressed as cubic centimeters of the decinormal silver. The last column gives the transport number (H) of the chlorine, computed by the formula

$$H = 0.0108\ L/W.$$

When two tubes were electrolyzed in series with the same solution in each, the numbers in the first four columns are the same for each, and are not repeated in the table. The fourth and twelfth electrolyses in the KCl series were carried out in series with each other; likewise the fifth and ninth.

These results show clearly that the transport numbers of the salts investigated are much lower in solutions containing acetone than in pure water, although they do not agree well enough among themselves to fix definitely the amount of the decrease.

In conclusion, I desire to express my thanks to Professor W. Lash Miller at whose suggestion these measurements were undertaken in the Spring of 1906, and to the authorities of the University of Toronto for the use of the electrochemical laboratory.

The University of Toronto,
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UNIVERSITY OF TORONTO STUDIES

PAPERS FROM THE CHEMICAL LABORATORIES

No. 73: THE CONDENSATION OF ACETONE WITH OXALIC ESTER, BY ROBERT H. CLARK

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[Mechanism of the Acetacetic Ester Synthesis. I.]

THE CONDENSATION OF ACETONE WITH OXALIC ESTER

BY ROBT. H. CLARK

Acetacetic ester was first prepared by Geuther,[1] in 1863, by the action of metallic sodium on ethyl acetate. It has since become one of the most important agents in organic synthesis; even in 1898 the bibliography of the ester and its derivatives, published by the Smithsonian Institution, occupied 148 pages.

Twenty-five years after Geuther's discovery, W. Wislicenus and L. Claisen showed that a large class of substances, chemically analogous to acetacetic ester, could be prepared by the action of metallic sodium or of sodium ethylate on esters, mixtures of esters, or mixtures of esters with ketones. They thus, in a sense, generalized Geuther's reaction; and their work has proved of the very greatest importance to chemistry, both pure and applied.

These discoveries led Claisen to a new theory of the formation of acetacetic ester; or, to be more accurate, it was the desire to put his new theory to the test that led to his experimental discoveries.

Kolbe,[2] and after him v. Baeyer,[3] explained the formation of acetacetic ester from ethyl acetate by assuming the primary formation of a sodium- or disodium-acetic ester, $CH_2Na.COOEt$, or $CHNa_2.COOEt$; and this theory in Baeyer's hands led to the synthesis of phlorogluein from sodium malonic ester, a most important step in his classical work on the constitution of benzene.

Claisen[4] rejected this view, and suggested in its place that Geuther's reaction is due not to the direct action of

[1] Göttinger Anzeigen, 1863, 281.
[2] Zeit. f. Chem., 10, 637 (1867).
[3] Ber. chem. Ges. Berlin, 18, 3460 (1885).
[4] Ibid., 20, 651 (1887).

sodium, but to that of sodium ethylate, which forms an addition product with the ethyl acetate; and that this reacts with more of the ethyl acetate to form acetacetic ester, thus:

$$CH_3.COOEt + EtONa = CH_3.C(ONa)(OEt)_2.$$
$$CH_3.C(ONa)(OEt)_2 + CH_3.COOEt = CH_3.C(ONa):CH.COOEt + 2EtOH.$$

This theory of Claisen's has been generally accepted, but ever since its first appearance it has been attacked by Michael; the controversy between these two chemists on this subject has not even now come to a conclusion, and an important review of the argument by the latter has recently been published.[1]

Michael's principal argument against Claisen's views is based on the fact that while metallic sodium acts readily on ethyl acetate and gives a good yield of acetacetic ester, sodium ethylate acts only at high temperatures, and gives a poor yield. The fact that "absolute" ethyl acetate, from which the last traces of alcohol (that could serve to make sodium ethylate) have been removed, will not act with sodium at all, he classes with the numerous reactions that will not take place unless in presence of a trace of water—that between sulphuric acid and metals, for instance. And Claisen's "experimentum crucis," *viz.*, that isobutyric ester forms no condensation product analogous to acetacetic ester, he explains on grounds of his own.

Claisen, in reply, deals at length with the action of metallic sodium on ethyl acetate, pointing out that if merely a trace of alcohol be present the reaction begins slowly, and that the rate increases as the reaction proceeds and more alcohol is formed, according to the equation quoted above. This alcohol reacts with the sodium and produces the necessary ethylate. The unsatisfactory yield, when sodium ethylate itself is substituted for metallic sodium, he explains by stating that the reaction between sodium ethylate and ethyl acetate is reversible, and that the product is de-

[1] Ber. chem. Ges. Berlin, 38, 709 (1905).

composed by alcohol; if sodium is present, the alcohol formed by the reaction is at once decomposed, otherwise it accumulates and spoils the yield.

In defending his theory, Claisen thus perhaps unconsciously appeals to the principles of chemical kinetics and equilibrium; but his main argument is based on the analogy between the acetacetic ester synthesis and the condensations discovered by himself and Wislicenus. One explanation must do for all, he says; and that must be the ethylate explanation, for many of these condensations may be carried out successfully in dilute alcoholic solutions of that substance.

The methods of physical chemistry for attacking problems such as this, which deal with the mechanism of reactions, have all grown up since Claisen's first paper was published, and have not hitherto been applied to the elucidation of this particular question. It seemed, therefore, desirable to test the validity of Claisen's assumption that the condensation of esters with esters is identical with that of ketones with esters; and to see whether the results of kinetic measurements can be brought into line with his theory of the synthesis.

The reaction between ethyl oxalate and ethyl acetate was selected as typical of one group, and that between ethyl oxalate and acetone of the other. The present paper contains the results of my measurements on the rate of the latter, while Mr. H. C. Cooke is engaged with a study of the former reaction; the condensation of acetophenone with acetic ester is also being studied in this laboratory. It is proposed to publish the results of these investigations as they are obtained, and to postpone theoretical discussion until the material has been collected.

In investigations of this kind it is necessary to be provided with some means of stopping the reaction at will, and of determining the amount of change that has taken place. In the present case, the first end was attained by neutralizing the sodium ethylate, and the second by determining the depth of color produced by the addition of a solution of ferric chloride.

The feasibility of this method of analysis was ascertained only after a number of experiments with pure acetonoxalic ester and ferric chloride, and the unexpected nature of some of the facts disclosed during these experiments led to an extension of the study of this ferric reaction beyond the limits necessary for the foundation of an analytical method.

An account of my experiments on the ferric chloride reaction follows the description of the method employed in preparing the acetonoxalic ester, and is followed in turn by the measurements of the rate at which the latter substance is synthesized.

Preparation of Acetonoxalic Ester

The method of preparing this substance as given by Claisen[1] consists in adding a mixture of one mol each of acetone and oxalic ester to an alcoholic solution of one mol of sodium, boiling off the alcohol, and fractionating the ester in vacuo.

In my first attempts to follow these directions I got absolutely no yield, and even when the experiments were repeated with Merck's best acetone, Kahlbaum's absolute alcohol, and Kahlbaum's ethyl oxalate, the result was not much better. In the end, I found that the trouble was caused by the presence of traces of water in the "absolute" alcohol employed, and it was only when I discarded Kahlbaum's and Merck's preparations and worked with Squibb's that satisfactory results were obtained. This extreme sensitiveness of the reaction to water is not hinted at anywhere in the literature.

In the presence of a trace of water, sodium ethylate and oxalic ester in alcoholic solution give a whitish gelatinous precipitate, which is quickly formed and is quite distinct in appearance from the yellow denser precipitate of sodiume acetonoxalic ester. In my experiments I was even unable to empty the pipettes by blowing through them, for fear of the deleterious action of the water so introduced into the

[1] Ber. chem. Ges. Berlin, 20, 2189 (1887).

reacting mixture. A few quantitative measurements showing the effect of traces of water on the yield of acetonoxalic ester are given on page 11.

Instead of fractionating the ester, which I found to be accompanied by losses, I purified it by freezing; the following is a full description of my method of preparation: 58 grammes of acetone and 146 grammes of ethyl oxalate were mixed in a liter flask, and cooled in ice water; a solution of 23 grammes of sodium in 460 grammes of absolute alcohol was then slowly added. In the course of an hour the sodium compound had separated completely; it was freed from the mother-liquor by filtration through cheesecloth, and pressed between filter paper. The sodium compound was then weighed, and slightly less 30 percent sulphuric acid added than enough to neutralize the sodium present. An oil separates, which is dried in a vacuum over calcium chloride, and the acetonoxalic ester separated from it in the form of crystals by freezing in a bath of ice and salt. So prepared, the ester melts at 18°, and boils at 210° (thermometer in vapour) at a pressure of 753 mm.

Acetonoxalic Ester and Ferric Chloride

A series of preliminary experiments showed that the deep red colour produced by ferric chloride in solutions of acetonoxalic ester was not affected (when viewed longitudinally, through a column of liquid in a test-tube) by addition of water, alcohol, acetone or ethyl oxalate if the ferric chloride is in large excess, but that the colour grew fainter if sodium ethylate, or any alkali or acid was added; alkalies seemed to have more effect than acids. On warming, the tint grew darker, the original colour being restored on cooling, but a difference of ten degrees had little effect on the colour.

Colorimeter

A colorimeter was then set up, consisting of two small test-tubes of the same size and form, with flattened bottoms; one of them was provided with a side tube sealed on near the bottom, and served for the standard solution, the other took

the sample to be analyzed. Attached by rubber to the side tube was a glass tube of one centimeter bore, which could be moved up or down in front of a millimeter scale; the position of the meniscus on the scale gave the depth of the standard liquid in the tube.

The two tubes were enclosed, to prevent access of light from the side, and were slanted a little, so that the tops touched but the bottoms were about a centimeter apart; they were covered by a white card in which two small holes were made, so that on looking into the solutions the sides of the tubes could not be seen.

The whole apparatus was surrounded with ice water to prevent heat from the arc lamp (which served as source of light) from raising the temperature, and affecting the colour.

Measurements with this apparatus proved that if ferric chloride be present in sufficient excess, the depth of colour is directly proportional to the amount of acetonoxalic ester, provided that the readings are not made when the tubes are nearly empty. The following table shows the degree of accuracy attained.

In the table the first column gives the volume of F/250 acetonoxalic ester (dissolved in 1 percent alcohol);[1] the second and third, the height of the standard solution in millimeters in two sets of experiments, two settings were made in each case; while the fourth and fifth columns give the quotients, or the height in millimeters of the standard solution corresponding to 1 cc of the volumetric ester solution. When the reading is 38 or more, the quotient remains constant at 5.40 ± 0.05.

In pure solutions of acetonoxalic ester, therefore, the ferric reaction serves as basis for a satisfactory colorimetric determination; it remained to see whether any of the other chemicals present also gave a colour with iron. Acetone, or oxalic ester alone gave no colour; the sodium ethylate was neutralized before the iron was added; mixtures of sodium

[1] Containing 0.624 gram ester per liter, or approximately one formula weight in 250 liters.

ethylate and oxalic ester gave a reddish colour, but the tint was too faint to be measured in the colorimeter.

TABLE I

Ester	Colorimeter reading		Quotient	
	Set I	Set II	I	II
4cc	21 21	— —	5.02	—
6	32.5, 32.5	— —	5.04	—
7	37.5, 38.0	38.0, 38.0	5.4	5.4
8	44.0, 44.0	43.0, 44.0	5.5	5.4
9	49.0, 49.0	49.0, 49.5	5.4	5.4
10	55.0, 52.0	55.0, 55.0	5.35	5.5
11	60.5, 60.5	60.0, 60.5	5.5	5.5
12	65.0, 66.0	65.0, 66.0	5.4	5.4

Hence 0.000624 gram acetonoxalic ester gives 5.4 mm of standard colour.

The possible formation of acetondioxalic ester had also to be reckoned with, although the conditions prescribed in the instructions[1] for preparing this compound are very different from those obtaining in my experiments. I consequently prepared a quantity of this ester, and found that with ferric chloride in aqueous-alcoholic solution it gives various shades of brown. None of this compound appears to be formed in my experiments, but in the mixtures of acetonoxalic ester with 5 percent or so of acetondioxalic ester I was unable to detect the brown colour in the presence of the red either with the naked eye, or with a pocket spectroscope.

The colorimetric determination, after addition of ferric chloride, was consequently adopted as my method of analysis, and a standard colour was prepared by making up 2 cc of an F/2 solution of acetonoxalic ester (19.5 grams crystallized ester made up to 250 cc with Squibb's alcohol) and 25 cc ferric chloride solution[2] to one-quarter liter with water. The colour of this solution faded very slowly, but to obviate the

[1] Ber. chem. Ges. Berlin, 22, 3271 (1890).

[2] 81.3 grams of Merck's crystallized hydrate per liter.

possibility of errors from this source, the standard colour was made up fresh daily.

The Double Reading

Having thus provided myself with a method of analysis, I proceeded with the determinations of the rate at which acetone and ethyl oxalate react; but after a number of measurements had been made, I was surprised by an experiment in which the acetonoxalic ester present (measured as usual with the colorimeter) was just twice as much as could possibly be formed from the amounts of acetone and ethyl oxalate taken.

At first, of course, this looked liked a slip, but investigation showed that whenever excess of sodium ethylate had been used the readings were high. I then made a study of the reaction between sodium ethylate and my preparation of acetonoxalic ester, and found that when these two substances are brought together in equivalent quantities in absolute-alcohol solution, the mixture after neutralization with acid and addition of ferric chloride gives just twice the reading in the colorimeter that would have been obtained from the acetonoxalic ester employed without such treatment. If less than one equivalent of ethylate be added, the increase in colour is proportional to the amount added; excess of ethylate over one equivalent is without effect on the colour.

The colour matches nicely with the red of my standard solution. On dilution with water or alcohol, however, the colour fades, like that of ferric sulphocyanate, and in this respect differs from the standard.

The most remarkable thing about this new reaction, however, is that if ethyl oxalate be added to the alcohol solution after treatment with the ethylate the single, instead of the double, reading is obtained. The reactions in alcoholic solution between sodium ethylate and acetonoxalic ester, and between ethyl oxalate and the new substance are instantaneous.

Ferric Chloride and Other Keto-Esters

Compounds of ferric chloride with esters of the keto-acids have been studied by Geuther,[1] Bishop, Claisen and Sinclair,[2] Wislicenus,[3] Traube,[4] Knorr,[5] Morrel and Crofts,[6] and R. Schiff.[7] Geuther remarked the similarity between the colours produced by ferric chloride with acetacetic ester and with phenol, which he took as indicating similarity of structure between them; and, ever since, the presence or absence of the ferric reaction has been repeatedly discussed in the controversies over the enol and keto formulas for these esters, until at the present time the ferric reaction is generally accepted as the criterion for enolic constitution.

The reaction with sodium ethylate, which therefore might be interpreted as giving rise to a new enol group, seemed worth further consideration; and in reviewing the literature of acetacetic ester I found that in 1898 Robert Schiff[7] had already noted that traces of sodium ethylate enolize the keto form, in the case of the addition product of benzal-aniline and acetacetic ester, and that piperidine ketoizes the enol form; and from later experiments the author concludes that the reaction is quite general with this class of compounds.

My own investigations have shown that oxalacetic ester (prepared as described in *Liebig's Ann.*, **247,** 317) gives a red colour with ferric chloride, which is sharply *trebled* by treatment with sodium ethylate.

Acetacetic ester (Kahlbaum) gives a violet, which is unaffected by the ethylate treatment.

Methylacetacetic ester (Kahlbaum) was likewise unaffected. With regard to the "undoubling" by oxalic ester,

[1] Arch der Pharm., **116,** 97–110.
[2] Liebig's Ann., **281,** 344.
[3] Ibid., **291,** 147 (1896).
[4] Ber. chem. Ges. Berlin, **29,** 1718 (1896).
[5] Ibid., **30,** 2387 (1897).
[6] Jour. Chem. Soc., **73,** (1898).
[7] Ber. chem. Ges. Berlin, **31,** 601, 1388 (1898).

I find that in the case of acetonoxalic ester the same result is produced by the use of ethyl acetate.

The colour produced by ferric chloride in solutions of acetacetic ester resembles the "double" colour from acetonoxalic ester and the "treble" colour from oxalacetic ester, in being partially bleached by the addition of alcohol or water. It is therefore natural to suppose that the acetacetic ester from Kahlbaum's factory is in the same state as my acetonoxalic ester after treatment with sodium ethylate.

Before leaving this subject, I propose to compare the depth of the colour produced by ferric chloride in the solutions of the different esters, and see whether from this point of view also the acetacetic ester colour is comparable with the "double" colour from acetonoxalic ester. Of course, as the red compounds are not identical in the different cases, no very sharp results can be expected; they are, however, analogous, and preliminary experiments have shown me that the colour produced by ferric chloride in solutions of resorcin is closely twice that given by an equimolar solution of phenol.

The sharp doubling of the colour produced by ferric chloride with my specimen of acetonoxalic ester after previous treatment with sodium ethylate, would seem best accounted for by my compound having mono-hydroxyl constitution,

$$CH_3.CO.CH:C(OH).COOC_2H_5 \quad \text{or} \quad CH_3.C(OH):CH.CO.COOC_2H_5;$$

Perkin[1] and Gladstone, however, have concluded both from the magnetic rotation of the plane of polarization and the refractive power of a specimen of acetonoxalic ester supplied by Claisen that the constitution of the compound is represented by the dihydroxyl formula,

$$CH_3.C(OH):C:C(OH).COOC_2H_5.$$

Since this representation does not agree so well with my experiments, I determined the index of refraction of my compound to see if the two were identical.

[1] Jour. Chem. Soc., 61, 821 (1892).

The value given by Perkin and Gladstone for the sodium line is

$$n_D = 1.475699 \text{ at } 17°,^1$$

experimentally I found

$$n_D = 1.4750 \text{ at } 20°.$$

This measurement, together with the agreement in melting and boiling-points, leaves little doubt that my specimen of the ester was identical with that prepared by Claisen.

Boiling at atmospheric pressure for five minutes, and subsequent cooling, did not affect the refractive index, or the depth of colour with ferric chloride.

Attempts made to isolate a sodium salt corresponding to the "double" ferric salt, have not yet led to the desired conclusion, although sodium compounds have been isolated which contain a higher percent of sodium than the normal compound, and which give a colour with ferric chloride proportional to their content of sodium.

Effect of Water and of Alcohol on the Yield of Acetonoxalic Ester

The great effect exerted by traces of water on the yield has already been referred to (p. 5); the following table gives the results of experiments carried out with alcohol to which measured amounts of water had purposely been added.

Equivalent quantities of the three reagents, *viz.*, 0.50 cc ethyl oxalate, 0.27 cc acetone, 2.10 cc alcoholic solution of sodium ethylate (1.74 normal) and 2.13 cc alcohol—making a total volume of 5.0 cc—were mixed and the reaction allowed to proceed to completion. In the first experiment Squibb's alsolute alcohol was used, in the others a solution of water in alcohol; the weight and the volume percent of the water in the 5 cc of reaction mixture is given in the table. Under "yield" is entered the amount of acetonoxalic ester formed in percent of that theoretically possible.

[1] Jour. Chem. Soc., 61, 855 (1892).

TABLE II*a*

Water present		Yield
Grams	Vol. percent	Percent
0	0	96
0.0107	0.213	69
0.0146	0.291	56
0.0320	0.639	34
0.0426	0.852	20
0.0533	1.065	10
0.0639	1.278	7.5

In studying the effect of alcohol on the yield, it was, of course, impossible to keep the volume constant; addition of alcohol was therefore necessarily attended by retardation of the rate of condensation. That the yield also was reduced is shown by the experiments of the following table:

TABLE II*b*

Acetone cc	Oxalate cc	Ethylate cc	Total vol.	Time	Yield Percent
0.27	0.50	2.10	2.87	1 hour	100
"	"	"	5.00	2 days	100
"	"	"	10.00	2 "	70
"	"	"	10.00	28 "	72
"	"	"	20.00	28 "	57 & 58[1]
0.54	0.50	2.10	3.14	1 hour	100
"	"	"	5.00	2 days	100
"	"	"	10.00	28 "	75 & 77
"	"	"	20.00	28 "	62
0.27	1.00	2.10	3.37	1 hour	100
"	"	"	5.00	2 days	100
"	"	"	10.00	28 "	74 & 77
"	"	"	20.00	28 "	58 & 60

The results recorded in Table II suggested the possibility that sodium acetonoxalic ester might be decomposed by alcohol, as Geuther found sodium acetacetic ester to be. The mixture whose composition is given in the first line of Table II (which gives a hundred percent yield in an hour)

[1] Duplicates.

was accordingly made up, and after standing an hour and a half was diluted with alcohol, replaced in the thermostat (at 0° C), and analyzed after standing the time entered under "time" in Table III.

TABLE III

Volume	Time	Yield Percent
2.82 cc	0	100
5.00	11 hours	96
10.00	41 "	92
20.00	11 "	92
30.00	40 "	91
40.00	38 "	94

When the alcohol was first added, the sodium compound was stirred up with the solution by a dry rod, and the tube and contents were well shaken from time to time.

These experiments seem to show that the reaction studied in this paper is a reversible one, although it is clear that the equilibrium has not been attained in the experiments of Table III. A complete study of the reaction therefore involves measurements of the rate of condensation, the rate of alcoholysis, and the conditions of equilibrium. The present paper deals with the first of these only.

C. The Rate of Formation of Acetonoxalic Ester

The chemicals used in these measurements, and in those of Tables I, II and III, were:

Acetone.—Kahlbaum's "aus der Bisulfitverbindung."

Ethyl Oxalate, from Eimer & Amend, neutral.

Alcohol.—Squibb's absolute.

Acetonoxalic Ester, prepared as described on p. 5. Melting-point, 18° C; boiling-point, 210° C.

Ferric Chloride, Merck's C. P.

Sodium Ethylate.—For the preliminary experiments, a stock of the ethylate solution was prepared by dissolving sodium in alcohol, and kept in an atmosphere of hydrogen

generated electrolytically from a solution of caustic potash. On standing, however, the solution turned brown, and gave results different from those with a fresh preparation. In the end, I found it best to make up a fresh solution daily; the concentration was determined by titration with normal sulphuric acid, using methyl orange as indicator.

Method of Working

The reagents were measured into large test-tubes (150 cc) closed with rubber stoppers, and placed in a thermostat at zero. A separate mixture was used for each analysis, for fear of introducing water. The sodium ethylate pipette was washed with water and dried with a hot air-blast before each measurement.

When it was desired to stop the reaction, a measured volume of water was added, whereupon the caustic soda (formed from the ethylate and from the sodium-aceton-oxalic ester) promptly saponified the excess of oxalic ester, and was itself neutralized in the process; as one mol of the ester will thus neutralize two of the ethylate, it was not necessary to add additional ester except when an excess of ethylate had been used in making up the reacting mixture. After the caustic soda has been neutralized the ethyl oxalate is very slowly saponified, and thus makes the solution only slightly acid.

A known fraction of the aqueous alcoholic solution was then removed, mixed with 4 cc of the ferric chloride,[1] and compared with the standard in the colorimeter; enough of the reaction product was taken in each case to bring the reading between 30 and 50 mm. Two or three settings of the colorimeter were made in each case; and from three to eight samples of each reacting mixture were pipetted out and analyzed, depending on the agreement between the results, and on the ease with which I found I could decide on the end-point—that is to say, no doubt, on the state of my eyes.

[1] See foot-note, p. 7.

The results of these rate measurements are presented in tables, at the head of each of which are given the initial quantities of the reagents in milligramme-formula-weights, and the volume of the reacting mixture; in cubic centimeter under t the duration of the reaction in hours; under x the amount of acetonoxalic ester formed in milligramme-formula-weights; and under x *per liter* the amount of acetonoxalic ester formed per liter expressed in the same units. The values of x were calculated as follows:

$$x = \frac{\text{(color reading)} \times \text{(vol. after adding water)}}{\text{(vol. analyzed)} \times 5.4 \times 250}$$

In Tables IV–IX to "vol. after adding water" was 40 cc.

The experiments show that the powers of the concentrations to which the rate of condensation is proportional depend upon the degree of dilution by alcohol. In Tables IV–IX (vol. 20 cc) the rate is proportional to the first power of the concentration of the acetone, and to about the 1.2 power of the concentrations of the oxalic ester and of the ethylate. On diluting the same amounts of the three reagents to a volume of 30 cc the powers become 1, 1.75, 1.75 respectively; and on further dilution to 40 cc (Tables X–XVI) and to 50 cc (Tables XVII–XX) while still proportional to the concentration of the acetone, the rate is found to vary with the square of the concentrations of the oxalic ester and of the ethylate respectively.

This difference between the behaviour of acetone on the one hand, and that of the other two reagents on the other, lends support to Claisen's formulation of the condensation if it be supposed that the addition product assumed by him is largely dissociated in alcoholic solution. To account for the second powers of the concentrations met with at the higher dilutions, however, the addition product must be given twice the molecular weight assumed by Claisen.

Tables IV–IX give the experimental results without any attempt to represent them by a differential equation. For

the experiments of Tables X–XX, however, I have calculated the velocity constants of the equations

$$dx/dt K_1(A-x)(B-x)^2(C-x)^2 - K_2x(D-x) \quad \text{Equation 1}$$
$$dx/dt K_1(A-x)(B-x)^2(C-x)^2 - K_2x^2(D-x)^2 \quad \text{Equation 2}$$

from each successive pair of measurements by means of the "Method of Areas."

Equation 1 gave fairly constant values for K_1 but mostly negative—and therefore impossible—values for K_2; in some cases the values of K_2 were much greater than those of K_1 although the rate of condensation is obviously much greater than that of alcoholysis.

The numbers calculated from Equation 2 are more satisfactory, and are entered in the tables; in looking them over, it must be remembered that a small change in K_1 causes a large change in K_2.

The form of these equations was suggested by the experiments of p. 13; whatever hypothesis as to the mechanism of the reaction may ultimately be adopted, the constants entered in the tables may serve as the basis of a useful interpolation formula connecting the rate with the composition of the reacting solution.

My thanks are due to Prof. W. Lash Miller, at whose suggestion this research was undertaken, and under whose supervision it was carried out. The experiments were concluded in the summer of 1906.

TABLE IV

Acetone 3.7 Oxalic ester 3.7 Sodium ethylate 3.7 Vol. 20

t	Series I			Series II			Series III		
	"Vol. anal."	Readings	x	Vol. anal"	Readings	x	"Vol. anal"	Readings	x
0.25	10.0	34.5; 34; 35.0	0.102	10.0	32; 31; 31	0.093	10	34.0; 34; 33.0	0.099
0.50	6.0	43.0; 43; 42.0	0.210	5.0	32; 32; 31	0.187	5	34.0; 34; 33.0	0.199
0.75	4.0	39.0; 41; 40.0	0.296	4.0	37; 37; 37	0.275	4	39.0; 38; 39.5	0.289
1.00	3.5	45.0; 45; 44.0	0.378	3.0	35; 35; 35	0.348	3	36.0; 36; 36.0	0.355
1.50	2.5	47.0; 48; 47.5	0.563	2.0	34; 33; 34	0.496	2	35.0; 35; 35.0	0.518
2.00	2.0	45.0; 45; 45.0	0.667	2.0	42; 42; 42	0.626	2	47.5; 48; 47.0	0.629
3.00	—	— — —	—	1.5	42; 42; 42	0.829	1	30.0; 30; 30.0	0.867
4.00	—	— — —	—	1.5	50; 51; 50	1.000	1	35.0; 35; 35.0	1.037

TABLE V

Acetone 7.4 Oxalic ester 3.7 Sodium ethylate 3.7 Vol. 20

t	Series I			Series II			Series III		
	"Vol. anal."	Readings	x	"Vol. anal."	Readings	x	"Vol. anal."	Readings	x
0.25	5	34.0; 34; 34.0	0.203	5.0	31; 31.0; 31.0	0.183	5.0	32; 32; 33.0	0.192
0.50	5	64.0; 63; 63.0	0.375	4.0	48; 49.0; 47.0	0.355	3.0	37; 38; 37.0	0.370
0.75	3	52.0; 51; 51.5	0.511	3.0	50; 49.0; 49.5	0.489	—	— — —	—
1.0	2	44.0; 45; 44.5	0.659	2.0	43; 43.0; 43.0	0.637	1.5	33; 32; 33.0	0.644
1.5	1	31.5; 31; 31.0	0.925	2.0	57; 58.0; 57.0	0.852	1.5	43; 43; 43.5	0.851
2.0	1	38.5; 39; 39.0	1.140	1.0	34; 35.5; 33.0	0.993	1.0	34; 35; 34.0	1.018
3.0	—	— — —	—	1.0	43; 42.0; 42.0	1.260	1.0	43; 43; 42.5	1.270
4.0	—	— — —	—	0.75	35; 36.0; 36.0	1.400	1.0	46; 46; 47.0	1.400

TABLE VI

Acetone 3.7 Oxalic ester 7.4 Sodium ethylate 3.7 Vol. 20

t	Series I			Series II			Series III		
	"Vol. anal."	Readings	x	"Vol. anal."	Readings	x	"Vol. anal."	Readings	x
0.25	4	33.0; 33; 32.5	0.243	5.0	38; 38; 37.5	0.223	5.0	40; 40; 40.0	0.237
0.50	3	43.0; 43; 44.0	0.429	4.0	59; 59; 59.0	0.437	4.0	60; 60; 60.5	0.445
0.75	2	43.0; 43; 44.0	0.642	3.0	68; 67; 66.0	0.661	3.0	66; 67; 66.0	0.656
1.0	2	54.5; 55; 55.0	0.811	2.0	58; 57; 57.0	0.851	2.0	56; 56; 56.0	0.830
1.5	1	36.0; 37; 37.0	1.089	1.5	56; 56; 56.5	1.110	1.5	59; 58; 58.0	1.155
2.0	1	46.0; 46; 45.0	1.355	1.0	46; 46; 46.0	1.360	1.0	47; 47; 48.0	1.400
3.0	—	— — —	—	1.0	54; 54; 53.0	1.648	1.0	55; 55; 55.0	1.629
4.0	—	— — —	—	0.75	42; 42; 42.0	1.679	0.75	43; 43; 43.0	1.702

TABLE VII*

Acetone 3.7 Oxalic ester 3.7 Sodium ethylate 7.4 Vol. 20

t	Series I			Series II			Series III		
	"Vol. anal."	Readings	x	"Vol. anal."	Readings	x	"Vol. anal."	Readings	x
0.25	3	50; 49.0; 49.5	0.244	3	48.0; 48; 48.0	0.237	3	46.5; 47; 46.0	0.229
0.50	2	62; 62.5; 63.0	0.463	2	65.0; 65; 65.0	0.482	2	60.0; 60; 60.0	0.445
0.75	1	40; 40.0; 40.0	0.593	1	37.5; 38; 38.0	0.555	1	37.5; 38; 38.0	0.555
1.0	1	55; 55.0; 55.0	0.815	1	51.0; 50; 50.0	0.750	1	47.0; 48; 48.0	0.704
1.5	0.75	50; 50.0; 49.5	0.981	0.75	47.0; 47; 46.5	0.926	0.75	46.0; 47; 47.0	0.926
2.0	0.75	56; 56.0; 56.5	1.110	0.75	58.0; 58; 58.5	1.148	0.5	39.0; 39; 39.5	1.160
3.0	—	— — —	—	0.5	50.0; 50; 50.0	1.480	0.5	51.0; 52; 51.0	1.526
4.0	—	— — —	—	0.5	62.0; 61; 62.0	1.810	0.5	62.0; 61; 61.0	1.810

* On account of the double reading (see p. 8) in Tables VII, XIII and XX the readings have been halved in calculating x. See also Table XIII*b*.

TABLE VIII

Acetone 11.1 Oxalic ester 3.7 Sodium ethylate 3.7 Vol. 20

t	"Vol. anal."	Readings	x
0.25	4.0	42.0; 42.0; 42.0	0.311
0.50	3.0	52.5; 53.0; 52.0	0.518
0.75	2.0	45.5; 45.5; 45.5	0.674
1.0	1.5	41.5; 42.0; 42.0	0.822
1.5	1.0	36.0; 36.0; 36.0	1.067
2.0	0.75	32.0; 31.0; 31.5	1.245
3.0	0.75	40.0; 41.0; 40.0	1.595

TABLE IX

Acetone 3.7 Oxalic ester 11.1 Sodium ethylate 3.7 Vol. 20

t	"Vol. anal."	Readings	x
0.25	3.0	34.0; 34.0; 35.0	0.341
0.50	2.5	52.0; 52.0; 52.0	0.616
0.75	1.25	40.0; 39.0; 40.0	0.939
1.0	1.0	40.0; 40.0; 39.5	1.178
1.5	0.75	40.0; 41.5; 41.0	1.622
2.0	0.6	39.5; 40.0; 40.5	1.970
3.0	0.5	38.5; 39.0; 39.0	2.290

TABLE X

Acetone 3.7 Oxalic ester 3.7 Sodium ethylate 3.7 Vol. 40

t	x	x per liter	$K_1 \times 10^{12}$
4.0	0.069	1.725	—
6.5	0.115	2.875	68
16.0	0.272	6.80	74
24.0	0.385	9.525	67
35.0	0.500	12.50	69
40.0	0.563	14.075	79
48.0	0.593	22.05	66
72.0	0.882	31.00	80
120.0	1.240	37.00	80
192.0	1.481	47.00	86
—	1.888	—	—
		Average	74

TABLE XI

Acetone 7.4 Oxalic ester 3.7 Sodium ethylate 3.7 Vol. 40

t	x	x per liter	$K_1 \times 10^{12}$	K_2
4	0.122	3.05	—	—
8	0.244	6.10	—	—
16	0.467	11.67	57	11×10^{-13}
24	0.607	15.17	56	36×10^{-13}
35	0.741	18.52	48	13×10^{-13}
40	0.800	20.00	42	10×10^{-13}
48	0.860	21.50	40	—

TABLE XII

Acetone 3.7 Oxalic ester 7.4 Sodium ethylate 3.7 Vol. 40

t	x	x per liter	$K_1 \times 10^{12}$	K_2
4	0.250	6.25	—	—
8	0.459	11.47	72	—
16	0.778	19.45	80	14×10^{-13}
24	0.964	24.10	78	11×10^{-13}
35	1.112	27.80	73	7×10^{-13}
40	1.169	29.22	63	5×10^{-13}
48	1.259	31.47	69	4×10^{-13}
72	1.511	37.77	64	3×10^{-13}
120	1.837	45.92	55	—
240	2.192	54.80	—	—
—	2.222	55.50	—	—

TABLE XIII

Acetone 3.7 Oxalic ester 3.7 Sodium ethylate 7.4 Vol. 40

t	x	x per liter	$K_1 \times 10^{12}$	K_2
4	0.280	7.00	—	—
8	0.426	10.65	73	—
16	0.611	15.27	58	20×10^{-13}
24	0.778	19.45	53	4×10^{-13}
35	0.964	24.10	52	3×10^{-13}
40	1.037	25.92	55	3×10^{-13}
48	1.111	27.77	52	4×10^{-13}
72	1.288	32.20	49	3×10^{-13}
120	1.518	37.95	42	3×10^{-13}
168	1.741	43.92	41	2×10^{-13}
192	1.837	45.92	41	—
—	2.185	54.62	—	—

TABLE XIV

Acetone 11.1 Oxalic ester 3.7 Sodium ethylate 3.7 Vol. 40

t	x	x per liter	$K_1 \times 10^{12}$	K_2
4	0.177	4.42	41	—
8	0.311	7.77	56	—
16	0.591	14.77	61	—
24	0.829	20.72	63	—
35	1.036	25.90	70	20×10^{-13}
40	1.118	27.95	77	—
48	1.215	30.37	74	—
		Average	64	

TABLE XV

Acetone 3.7 Oxalic ester 11.1 Sodium ethylate 3.7. Vol. 40

t	x	x per liter	$K_1 \times 10^{12}$	K_2
4	0.433	10.82	—	—
8	0.813	20.32	60	—
16	1.301	32.52	60	—
24	1.481	35.02	59	—
35	1.735	43.37	69	—
48	1.895	47.37	68	5×10^{-13}
72	2.104	52.60	63	1×10^{-13}
120	2.385	58.62	67	—

TABLE XVI

Acetone 3.7 Oxalic ester 3.7 Sodium ethylate 11.1 Vol. 40

t	x	x per liter	$K_1 \times 10^{12}$	K_2
4	0.444	11.00	56	—
8	0.814	20.35	63	—
16	1.259	31.47	74	13×10^{-13}
24	1.408	35.20	63	—
35	1.660	41.50	63	—

TABLE XVII

Acetone 3.7 Oxalic ester 3.7 Sodium ethylate 3.7 Vol. 50

t	x	x per liter	$K_1 \times 10^{12}$	K_2
12	0.145	2.90	38	320×10^{-13}
24	0.288	5.66	37	—
36	0.429	8.58	45	73×10^{-13}
48	0.518	10.36	45	93×10^{-13}
72	0.711	14.22	46	33×10^{-13}
96	0.837	16.74	47	40×10^{-13}
120	0.922	18.44	46	33×10^{-13}
144	1.000	20.00	46	31×10^{-13}

TABLE XVIII

Acetone 7.4 Oxalic ester 3.7 Sodium ethylate 3.7 Vol. 50

t	x	x per liter	$K_1 \times 10^{12}$	K_2
12	0.244	4.88	34	—
24	0.459	9.18	37	15×10^{-13}
36	0.615	12.30	36	5×10^{-13}
48	0.741	14.82	33	—
72	1.007	20.14	38	3×10^{-13}
96	1.155	23.10	38	3×10^{-13}
120	1.260	25.20	38	3×10^{-13}
144	1.518	30.36	—	—

TABLE XIX

Acetone 3.7 Oxalic ester 7.4 Sodium ethylate 3.7 Vol. 50

t	x	x per liter	$K_1 \times 10^{12}$	K_2
12	0.377	7.54	27	—
24	0.703	14.06	30	—
36	0.941	18.82	33	10×10^{-13}
48	1.081	21.62	32	9×10^{-13}
72	1.260	25.20	29	4×10^{-13}
96	1.452	29.04	28	2×10^{-13}
120	1.592	31.84	30	4×10^{-13}
144	1.604	32.08	—	—

TABLE XX

Acetone 3.7 Oxalic ester 3.7 Sodium ethylate 7.4 Vol. 50

t	x	x per liter	$K_1 \times 10^{13}$	K_2
12	0.400	8.00	30	1×10^{-13}
24	0.702	14.04	30	—
36	0.923	18.46	32	9×10^{-13}
48	1.080	21.60	30	2×10^{-13}
72	1.306	26.02	25	1×10^{-13}
120	1.581	31.62	26	1×10^{-13}
144	1.702	34.04	27	1×10^{-13}

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CXXX.—*Some Esters of Arsenious Acid.*

By William Robert Lang, John Francis Mackey, and Ross Aitken Gortner.

J. M. Crafts (*Bull. Soc. chim.*, 1870, [ii], **14**, 99), in referring to the existence of compounds of arsenic with alcohol radicles, pointed out that no esters of arsenious or of arsenic acid had been prepared up to the year 1870, and described a method by which he obtained ethyl, methyl, and amyl arsenates; this consisted in heating the corresponding iodides in sealed tubes at 100° with normal silver arsenate. The esters were purified by washing with ether and distilling under diminished pressure. They are liquids of high boiling

point, above 200°, and suffer partial decomposition if distilled under atmospheric pressure; in the case of the amyl arsenate so much so that he found it impossible to obtain it pure even when distilled in a vacuum. The addition of water to them causes immediate and complete decomposition into arsenic acid and the alcohol. Crafts determined their composition by weighing the precipitated arsenic acid as the magnesium salt and the carbon and hydrogen by combustion, and gave them the formula R_3AsO_4. For the arsenites of the alkyl radicles he used three methods, a sealed tube being employed: (1) the interaction of arsenious oxide and ethyl silicate at 200°, (2) the interaction of ethyl iodide and silver arsenite at 150°; and (3) the interaction of arsenic bromide and sodium ethoxide, which last method he considered the best, although in it a secondary reaction between the ester formed and the sodium ethoxide causes a condition of equilibrium to be set up, and no more ester is formed.

It is to be noted that even if disodium hydrogen arsenite is employed the resulting arsenite is always the trialkyl salt. Crafts states that arsenious oxide and alcohol do not react when heated in a sealed tube, nor does arsenious oxide either with ether alone or with the addition of ethyl acetate, even when in contact for twenty hours.

These esters prepared by Crafts are specified by Auger (*Compt. rend.*, 1902, **134**, 238) as the only ones known, and he refers in a later paper (*Compt. rend.*, 1906, **143**, 907) to Crafts' inability to obtain any ester by heating the alcohols and oxides of arsenic in a sealed tube. Auger bases his conviction that an ester is produced on the fact that arsenious oxide is volatile in alcohol vapour, although not in water vapour, and concludes that this cannot be accounted for unless there is an ester formed.* Also he succeeded in preparing an ester from glycerol and arsenic oxide, and from ethyl, methyl, *iso*propyl, *iso*butyl, and *iso*amyl alcohols and arsenious oxide. He heated the alcohols with crystalline arsenious oxide for some hours, evidently in a sealed tube, as the temperatures quoted are far above the boiling points of the alcohols, and gives 6·5 per cent. as the extreme limit of esterification in the case of methyl alcohol, and 1·2 per cent. in that of ethyl alcohol. Calculating from his figures, the yield of ester for the higher alcohols appears to be 2·62 per cent., 0·25 per cent., 1·00 per cent., and 0·63 per cent. for propyl, *iso*propyl, *iso*butyl, and *iso*amyl alcohols respectively.

So far as can be gathered from the paper, Auger takes no account of the extreme solubility, as we have found, of arsenious oxide in the ester. These small yields and the difficulty found by Crafts in

* We have passed the vapour of methyl alcohol over arsenious oxide heated in a long tube, and the ether obtained differs entirely from methyl arsenite.

obtaining any results from the action of the acid on the alcohol are evidently due to the reversal of the reaction:

$$6ROH + As_2O_3 = 2R_3AsO_3 + 3H_2O \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Auger states that he removed the water as it was formed by fractional distillation (in the case of *iso*butyl and *iso*amyl esters), or by passing the mixture of alcohol and water vapour over calcium carbide placed in an adapter, thus removing the water and allowing the alcohol to drop back into the flask in which the reaction takes place. An excellent yield, how much is not stated, of propyl, *n*-butyl and *iso*butyl arsenites was thus obtained. Phenol, in the same way, yielded an ester hitherto only prepared by the action of sodium phenoxide on arsenic trichloride.

The nature of the reaction expressed by equation (1) and the properties of the ester clearly show that only by removing the water as it is formed can one expect to get a large yield. Our work has been done in two ways, namely, by heating the mixture in a vessel to which is attached a modified Soxhlet tube and condenser, the Soxhlet containing anhydrous copper sulphate, and by adding this dehydrating agent directly to the mixture. A comparison of the yields obtained is given in the sequel. By these two methods yields of from 14·8 per cent. (cold) to 58·6 per cent. (hot) have been obtained with aliphatic alcohols, and with the phenols as high as 90 per cent. Experiments have also been made, with very encouraging results, on benzyl alcohol and on esters of hydroxy-acids. We hope to show that the use of such a dehydrating agent as copper sulphate in a Soxhlet tube will allow of the preparation of a series of esters from the oxides and possibly sulphides of arsenic, antimony, tin, and perhaps bismuth with compounds containing hydroxyl, where the boiling points of such esters are higher than that of water, as, indeed, is the case with all of these; also with anhydrous copper sulphate in contact with the substances themselves. In many preparations, too, of esters generally and allied products, the formation of water in the reaction produces an equilibrium resulting in a very low yield. It is expected that by removing this water, as is done in the instances described in the present paper, the yields will be greatly increased in many commercial processes.

Experimental.

Heating with Inverted Condenser only.—Weighed quantities of propyl, *iso*butyl, and *iso*amyl alcohols were mixed with excess of arsenious oxide and heated with a direct flame for forty-five minutes in a flask to which a reflux condenser was attached. The clear liquid obtained was poured off from the excess of arsenious oxide and fractionated under diminished pressure. The esters so purified were

analysed and the yield compared with that calculated from equation (1).

Our method of ascertaining the composition of the esters differs from that used by Auger.* The ester was decomposed with water, forming arsenious oxide and liberating the alcohol. The arsenious oxide was dissolved in sodium carbonate and titrated with $N/10$ iodine (a preliminary test having shown that the alcohol did not react with iodine). By this means the quantity of arsenic in the ester was determined.

iso-*Amyl Arsenite.*—1·4 Grams were decomposed with 10 c.c. of water, sufficient sodium carbonate added to dissolve the arsenious oxide, and the whole diluted to 100 c.c.; 25 c.c. of this required 17 c.c. of standard iodine for oxidation, corresponding with 22·4 per cent. of arsenic. In 50 grams of the ester, the alcohol was determined and found to weigh 39 grams, or 78 per cent. *iso*Butyl and propyl arsenites were also analysed in a similar way:

Ester.	Per cent. As found.	Per cent. As calculated as $(RO)_3$ As.
Methyl	44·5	44·6
Ethyl	—	—
Propyl	29·6	29·7
*iso*Butyl	25·7	25·5
Amyl	22·2	22·3
*iso*Amyl	22·4	22·3

Expressing these as salts of arsenious acid, the formulæ become $(C_5H_{11})_3AsO_3$, $(C_4H_9)_3AsO_3$, and $(C_3H_7)_3AsO_3$.

Propyl arsenite is a yellow, mobile liquid boiling at 216° and decomposing very readily on addition of water.

iso*Butyl arsenite* is a deep yellow, mobile liquid of specific gravity 1·069; it decomposes rapidly in presence of water into *iso*butyl alcohol and arsenious oxide; under 760 mm. pressure it decomposes at 242°, and boils at 157° under 30 mm. pressure.

iso*Amyl arsenite* is a yellow liquid of specific gravity 1·050; it boils at 185° under 30 mm. pressure, and under atmospheric pressure it decomposes at 284°; in the presence of water, it decomposes into *iso*amyl alcohol and arsenious oxide.

Heating with Soxhlet Attachment and Anhydrous Copper Sulphate.—To eliminate the water as it is formed and so increase the yield of ester, the conditions of the experiments were modified. One hundred and sixty grams of *iso*amyl alcohol were added to 70 grams of

* Auger determined the amount of arsenic in the cooled liquid obtained (a mixture of the ester and alcohol) by means of iodine. The difference between this and the amount of arsenious oxide that would dissolve in the same quantity of alcohol in the cold was taken as representing the amount of ester formed (*Compt. rend.*, 1906, **143**, 908). No account was taken of the solubility of arsenious oxide in the esters themselves.

arsenious oxide in a 300 c.c. flask. An ordinary Soxhlet tube was connected with the flask, and a condenser, fitted with a calcium chloride tube, was attached to the Soxhlet, which contained a large filter paper filled with anhydrous copper sulphate. The liquid in the flask was heated to boiling, and the water formed was absorbed by the anhydrous copper sulphate, which turned blue as soon as the first drops of condensed liquid fell on it. Heating was stopped after forty-five minutes, when small rings of a compound of high boiling point began to form on the sides of the flask; after cooling, the clear product was filtered and fractionated under diminished pressure. 110·25 grams of ester were obtained, being a yield of 58·6 per cent. as compared with 13·22 per cent. obtained without the use of a dehydrating agent.

In similar experiments with *iso*butyl and propyl alcohols, yields of 56·25 per cent. and 56·75 per cent. respectively were obtained, as compared with 11·09 and 8·79 per cent. when no dehydrating agent was employed.

Use of Dehydrating Agent in the Cold.—The esterification of these three alcohols by arsenious oxide can be carried out even in the cold if a dehydrating agent is used; 120 grams of the alcohol were shaken in a stoppered bottle at room temperature with 60 grams of arsenious oxide and 70 grams of anhydrous copper sulphate for three days. The following yields were obtained: *iso*amyl arsenite, 17·2 per cent.; *iso*butyl arsenite, 15·8 per cent.; propyl arsenite, 14·8 per cent.

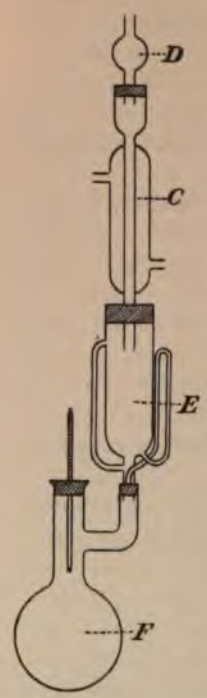
The following table indicates the comparative yields (per cent.) by different methods:

Ester.	Auger (in sealed tube).	Reflux condenser.	With anhydrous copper sulphate: in Soxhlet.	in the cold.
Methyl	6·5	—	33·8*	—
Ethyl	1·2	—	4·5*	—
Propyl	2·62	8·79	56·75	14·8
*iso*Butyl	0·25	11·09	56·25	15·8
Trimethylcarbinol	—	—	54·27	—
Amyl	1·00	—	54·00	—
*iso*Amyl	0·63	13·22	58·62	17·2

* The Soxhlet was not used, but the anhydrous copper sulphate was placed with the alcohol and arsenious oxide in a flask fitted with a reflux condenser.

A probable explanation of the low yield in the case of the ethyl arsenite lies in the fact that ethyl alcohol itself has a strong affinity for water which, for small quantities of water present, cannot be overcome by the anhydrous copper sulphate. This is readily shown by adding a drop of water to 5 c.c. of ethyl alcohol in which a little anhydrous copper sulphate has been placed. The copper sulphate is apparently not affected, whilst in the case of the higher alcohols a blue colour appears almost instantly, showing the hydration of the

copper sulphate. Methyl alcohol does not respond to this test as readily as do the higher alcohols, but it responds more readily than does ethyl alcohol. The yield in each case, using the copper sulphate, probably bears a direct relation to the respective affinities of the alcohol and of the copper sulphate for the water of the reaction. If a substance could be used which had a greater dehydrating power and at the same time was insoluble in alcohol, a higher yield would doubtless be obtained. Calcium carbide (Auger, *Compt. rend.*, 1906, **143**, 908) is not such a material: we have compared the yields obtained by replacing the anhydrous copper sulphate in the Soxhlet with fresh calcium carbide, using various alcohols, and the highest yield was in the case of *iso*amyl alcohol where 40·2 per cent. of ester was obtained after two hours' heating.



Esters obtained with Phenol and its Homologues.

For the esterification of these with arsenious oxide a side-necked flask was used the neck of which was bent upwards and attached to the Soxhlet, leaving the mouth of the flask free to receive a thermometer (see figure).

Phenyl Arsenite.—Weighed quantities of phenol (140 grams) and arsenious oxide (80 grams) were heated together, and in all cases it was observed that the reaction began at 100°, the mixture boiling violently at that temperature. The thermometer gradually rose to 133°, when a thick cloud formed in the flask. The temperature remained constant at that point for a few minutes and then gradually rose to a maximum, where it was kept for about five minutes: the heating was then stopped and the contents of the flask allowed to cool. The mixture of phenol, ester, and arsenious oxide, the latter of which is very soluble in the ester, was shaken with benzene, causing the precipitation of the arsenious oxide dissolved in the ester. The mixture was then filtered and the benzene solution of the ester fractionated under diminished pressure. The benzene distilled at 20°, the phenol at 69°, and the ester at 305°. The ester, purified by redistillation, weighed 105 grams, representing a yield of 60 per cent. *Phenyl arsenite* is a deep yellow, viscous liquid with a specific gravity of 1·59; it freezes at 31°, and boils at 305° under a pressure of 30 mm. It dissolves readily in methyl alcohol, benzene, ethyl acetate, or chloroform, and decomposes on addition of water, but not

so readily as the fatty arsenites. It was found on analysis to correspond with the formula $(C_6H_5O)_3As$, or $(C_6H_5)_3AsO_3$.

o-, m-, *and* p-*Tolyl Arsenites.*—One hundred grams of each of the cresols were heated with arsenious oxide for thirty minutes in the apparatus previously described, the arsenious oxide being separated by benzene. The liquid was then fractionated, and the esters, after having been purified and analysed as in the case of the phenyl arsenite, were found to correspond with the formulæ $(C_6H_4Me)_3As$, or $(C_6H_4Me)_3AsO_3$.

Naphthyl Arsenite.—One hundred grams of naphthol were heated with 30 grams of arsenious oxide for thirty minutes and the arsenious oxide in the ester separated by means of benzene. As yet, however, the pure ester has not been isolated.

Benzyl Arsenite.—One hundred grams of benzyl alcohol were heated with 35 grams of arsenious oxide for thirty minutes. The maximum temperature was 240°. The clear liquid was decanted and 75 c.c. of benzene added, the arsenious oxide collected, and the filtrate fractionated under 30 mm. pressure. The *benzyl arsenite* distilled at 285°, suffering partial decomposition. Although in the case of the fatty alcohols a drying agent in the Soxhlet was essential to absorb the water formed and to allow only the alcohols themselves to drop into the mixture, no such device was necessary with the phenols, as practically no phenol or ester ever found its way further than the side tube of the Soxhlet. The water formed remained in this apparatus, there being never sufficient volume of liquid produced to cause the syphon attachment to come into play.

To ascertain if it was possible to obtain these esters without the removal of the water formed during the reaction, the same quantities of phenol, benzyl alcohol, *o*-, *m*-, and *p*-cresol respectively, as were used in the previous experiments, were heated with arsenious oxide in a flask fitted with a reflux condenser only, but in no case was any arsenite formed in quantities sufficient to enable it to be isolated.

Method of Analysis for Esters of Phenol and its Homologues.—To determine the composition of the esters, it was found necessary to distil them several times in order to remove all traces of arsenious oxide which is readily soluble in them, in some cases to the extent of 30 per cent. About 3 grams of the ester were decomposed by 5 c.c. of water and 10 c.c. of potassium hydroxide (containing 700 grams of potassium hydroxide per litre), and the whole diluted to 500 c.c. Two samples of 10 c.c. each were taken for analysis; to one sample standard iodine was added in excess, shown by the formation of a precipitate of tri-iodophenol and the appearance of a clear yellow solution, the temperature being kept at 65°. The mixture was then cooled, acidified with sulphuric acid, and diluted to 500 c.c. with

water. The excess of iodine in 100 c.c. of this was titrated against standard thiosulphate, using starch as indicator. The quantity of thiosulphate necessary, multiplied by five, represents the quantity of iodine used. This quantity, subtracted from the original amount of iodine added, gave the amount necessary to change both the phenol to tri-idophenol and the arsenious oxide to arsenic oxide. To determine the quantity of arsenious oxide present in the ester, an excess of standard potassium dichromate was added to the second sample and this excess was determined with standard ferrous sulphate. The ratio between the dichromate and iodine being known, the number of c.c. of iodine equivalent to the amount of dichromate used was found and subtracted from the total iodine obtained in the previous determination, the difference being the amount combined with the phenol. From these data the relative quantities of arsenious oxide and phenol, formed by decomposing the ester, were obtained, and the composition of the ester thus determined.

To test the accuracy of this method, estimations were made with weighed quantities of (*a*) phenol, (*b*) arsenious oxide, (*c*) a mixture of these.

(*a*) To 0·8826 gram of phenol, 5 c.c. of potassium hydroxide (700 grams per litre) were added and the whole diluted to 250 c.c. . .(1)

Ten c.c. of this solution were found to be equivalent to 25·75 c.c. of standard iodine.

(*b*) To 0·5 gram of arsenious oxide, 5 c.c. of the same potassium hydroxide were added and diluted to 250 c.c. . . . . (2)

Ten c.c. of this solution were found to be equivalent to 6·5 c.c. of standard iodine.

(*c*) To 10 c.c. of solution (1), 10 c.c. of solution (2) were added and found to require 32·30 c.c. of standard iodine.

Thus 10 c.c. of solution (1) required 25·75 c.c. of iodine, and 10 c.c. of solution (2) required 6·50 c.c. of iodine; in all 32·25 c.c. as compared with 32·30 c.c. when mixed, a difference which is well within the limits of experimental error.

In order to see if arsenious oxide can be determined accurately in the presence of phenol by means of dichromate, experiments similar to those made with iodine were carried out with it. Ten c.c. of solution (2) required 6·07 c.c. of dichromate, a mixture of 10 c.c. of (2) with 10 c.c. of (1) required 6·09 c.c. of dichromate, or an error of less than 0·3 per cent.

Properties of the Arsenites prepared from Phenol and its Homologu es.

	Phenyl arsenite.	Benzyl arsenite.	*o*-Tolyl arsenite.	*m*-Tolyl arsenite.	*p*-Tolyl arsenite.
Yield (per cent.)					
(*a*) with Soxhlet	60	100	96	94	95
(*b*) without Soxhlet	nil	nil	nil	nil	nil
Specific gravity	1·59	1·43	—	1·45	1·46
Refractive index *	—	1·572	—	—	—
Boiling point † under 30 mm.	305°	255°	—	346°	—
Freezing point	−31°	−36°	—	—	—
Colour	yellow	blue	dark brown	dark brown	brown

* The blanks indicate that the refractive index is greater than 1·62098, the limit of the prism used.

† Where the boiling point is not given it is above 360°.

All these esters are soluble in methyl and ethyl alcohols, ether, benzene, ethyl acetate, or chloroform, and are decomposed at once by water.

This method of esterification is being carried out with arsenious oxide and the dihydric and trihydric phenols, but the quantitative results are not yet ready. A successful attempt has also been made to form similar esters with hydroxy-acids, methyl salicylate being heated with arsenious oxide. The products of the reaction, namely, water and an oil, were driven up into the Soxhlet where the latter decomposed, liberating arsenious oxide. The oil boils at about the same temperature as the methyl salicylate and has an almost unbearable odour. When the dehydrating agent is used in the Soxhlet it is expected the new ester will readily be separated.

Experiments have also been tried with arsenious sulphide in place of the oxide and a small yield of an ester obtained, presumably of the composition R_3AsS_3, but the upper portions of the flask and the condenser became coated with the orange-coloured arsenious sulphide, showing that decomposition had occurred. The work is being continued.

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BY W. R. LANG AND J. O. WOODHOUSE

(Reprinted from The Journal of the Chemical Society, Vol. 93)

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CII.—*The Volumetric Estimation of Silver.*

By William Robert Lang and John Obins Woodhouse.

In this journal (Lang and Allen, Trans., 1907, **91**, 1370) there was described an apparatus for the estimation of sulphates and salts of barium based on the rapid clearing of turbid solutions in narrow tubes. The same apparatus was used to determine silver by standard sodium chloride with a view to improving on the well-known Gay-Lussac method, but great difficulty was experienced in determining the end-point, the silver solutions not clearing sufficiently rapidly. The

apparatus was therefore modified considerably, with the result that estimations of silver were done in half an hour with an average error of less than a-tenth of one per cent.

The principal differences from the former apparatus were the use of fine sand to retain the silver chloride precipitate, the replacement of the funnel by a short piece of thin-walled glass tubing, which enables the slightest opalescence to be easily observed, and the permanent attachment to an exhaust for washing the precipitate and solution down the tube.

A rubber cork, pierced with two holes, is inserted in a flask, *A*, of about 600 c.c. capacity. Through it passes a tube, *C*, of about 60 mm. diameter, fitted with a stopcock, *D*, and to its upper end is sealed about 4 cm. of a thin test-tube, *E*, of 1—1·5 cm. diameter. About 8 cm. from the lower end of the tube *C*, a plug of glass-wool is inserted and the remainder filled with sand, previously washed free

from impurities. The sand is held in its place by a second plug of glass-wool, and the curved piece of tubing, *B*, filled with glass-wool and attached to *C* by a small piece of rubber tubing. The curved portion may, of course, be sealed on, but in these circumstances is not so readily filled. This prevents the back suction from displacing the sand. Through the second hole in the cork a small piece of tubing passes, connected by a length of rubber tubing, *F.M*, to a three-way tap, *H*. *J* is a small hand aspirator to force a portion of the contents of *A* up the tube *C* for titration in *E*, whilst *K* leads to the exhaust pump. It is advisable to have a space between the tap *H* and the water pump, as this ensures there always being a ready vacuum available the moment the connexion is made through *H* to the flask.

The first set of experiments was made with quantities of a solution of silver nitrate of known strength, using *N*/10 sodium chloride in excess as precipitant, and titrating back with *N*/10 silver nitrate. A portion of the silver solution, equivalent to 0·5 gram of silver, is

placed in the flask *A* and diluted to about 100 c.c. with distilled water, 50 c.c. of the *N*/10 sodium chloride solution is then run into the flask directly, and the whole heated to boiling to coagulate the precipitated silver chloride.

N/10 Silver nitrate is then run in directly to the solution and precipitate up to within a few c.c. of the calculated amount necessary. The rubber cork with its attachment is replaced and the three-way tap, *H*, opened, and air drawn through the solution for a few minutes. This materially assists the settling of the precipitate. The tap is adjusted, and by means of the aspirator, *J*, some of the liquid and precipitate forced through the layer of sand and glass-wool * into *E*, which it reaches in a perfectly clear condition, the silver chloride being completely retained by the sand. A drop of *N*/10 silver nitrate is added, when a precipitate is formed, varying in intensity with the excess of salt still present. The liquid and precipitate are then sucked and washed down into *A*, and, if the thickness of the precipitate justifies it, about 1 c.c. of the silver solution is added *directly* to the contents of the flask. The stopper is again inserted, and the operation of forcing the mixture up into *E*, titrating, and washing down again, continued until no change is visible in the clear liquid, when a drop of the silver solution is added. The thin walls of *E* render the faintest opalescence readily observable, more particularly if a corresponding glass tube containing distilled water be used for comparison. The results of the first set of experiments are as follows:

In each case, 50 c.c. of silver nitrate solution were employed (=0·5 gram Ag) and 50 c.c. of a solution of sodium chloride added, each c.c. of which is equivalent to 0·01081 gram Ag. This corresponds with 50·0463 c.c. *N*/10 sodium chloride. On titrating back and calculating the amount of silver equivalent to the nett sodium chloride used by the sample, the errors varied from zero to +0·54 per cent. Each titration required twenty minutes.

In order to reduce this error, if possible, samples containing 1 gram of silver were taken, 100 c.c. of sodium chloride added (1 c.c.= 0·01081 gram Ag), and the excess titrated back with *N*/100 silver nitrate solution (table I).

As in analyses of silver alloys by Gay-Lussac's method, the precipitation is effected in the presence of free nitric acid, a series of experiments was carried out to ascertain the effect of varying proportions of acid. The volume of the solution containing 1 gram of silver was 100 c.c.; the amount of acid varied from 10 c.c. to 50 c.c., and the resulting errors from +0·094 to −0·216 per cent., the mean error being −0·0634 per cent., the presence of the nitric acid thus tending to make the precipitation more complete.

* Glass-wool and asbestos were found to be incapable of retaining the precipitate.

TABLE I.

Grams Ag employed.	$N/100$-$AgNO_3$ used to titrate back, in c.c.	Nett $N/10$-NaCl used, in c.c.	Equiv. to grams Ag.	Diff. in Ag found, in grams.	Error per cent.
1·0	72·00	92·8926	1·0032	0·0032	+0·32
1·0	76·20	92·4726	0·9987	0·0013	−0·13
1·0	75·05	92·5876	0·99994	0·00006	−0·006
1·0	73·20	92·7726	1·0019	0·0019	+0·19
1·0	72·30	92·8626	1·0029	0·0029	+0·29

Average error = +0·266 per cent. and 0·068 per cent. Mean error = 0·198 per cent.
Average time taken = 27 minutes.

To test the usefulness of this apparatus as applied to the practical estimation of silver in bullion, the usual conditions under which this is done by the Gay-Lussac method were adhered to, namely, 1 gram of pure silver dissolved in about 15 c.c. of nitric acid, 100 c.c. of $N/10$ sodium chloride added, and the excess titrated with $N/100$ silver nitrate. (When necessary, any excess of silver solution added was titrated with $N/100$ sodium chloride.)

The following table contains the results of these experiments, and the time taken:

TABLE II.

Grams Ag employed.	$N/100$-$AgNO_3$ used to titrate back, in c.c.	Nett $N/10$-NaCl used, in c.c.	Equiv. to grams Ag.	Diff. in Ag found, in grams.	Error per cent.
1·004	72·00	92·8926	1·0032	0·0008	−0·08
1·000	73·30	92·7626	1·0018	0·0018	+0·18
0·9994	74·75	92·6176	1·00027	0·00087	+0·087
1·0018	73·80	92·7126	1·00129	0·0005	−0·05
1·0034	73·00	92·7926	1·0021	0·0013	−0·13
1·0030	72·30	92·8626	1·0029	0·0001	−0·01
1·0035	72·30	92·8626	1·0029	0·0006	−0·06

Average error = −0·066 per cent. and +0·133 per cent.
Mean error = −0·067 per cent. Average time taken = 30 minutes.

It may be added that no excessive shaking up of the mixture is required other than sufficient to ensure proper mixing after each addition of the reagent.

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A paper read at the Thirteenth General Meeting of the American Electrochemical Society, at Albany, N. Y., April 30, 1908; President C. F. Burgess in the Chair.

COPPER ANODES IN CHLORIDE SOLUTIONS.

By Saul Dushman.

In the following paper I intend to give a summary of an investigation undertaken with the object of explaining the anomalous behavior of copper as anode in chloride solutions. Preliminary experiments showed that copper dissolved with a valency ranging from 1 to 2, according to the experimental conditions. It was observed that in concentrated hydrochloric acid solution, it dissolved as a univalent metal, while in more dilute solution the valency was greater, and finally attained a value of 2 for very dilute solutions. The particular concentration of hydrochloric acid at which the copper ceased to dissolve as purely univalent varied with the rate of stirring, rate of circulation, current density, and other factors. Increased stirring or circulation caused the metal to dissolve much more as cuprous, while increasing the current density, under otherwise constant conditions, increased the proportion of cupric.

Although several hypotheses could have been made to explain these experiments, the one chosen seems to be in best accord with the quantitative experiments described below. It is assumed that the copper anode dissolves by the action of the current in such a manner that, at the boundary between solution and electrode, the chemical equilibrium between the cupric and cuprous salts in hydrochloric acid solution is maintained.

The investigation therefore naturally divided itself into two parts: (a) Investigation of the chemical equilibrium, (b) determination of concentrations at the electrode in the electrolytic experiments. The chemical equilibrium between cuprous and cupric salts has been investigated by E. Abel,[1] R. Luther,[2]

[1] E. Abel, Zeit. f. Anorg. Chem., 26, 361.
[2] R. Luther, Zeit. f. Physik. Chem., 36, 385.

and Bodländer and Storebeck.[3] A large number of experiments performed by myself, in which the methods of analysis and manipulation were different from any of the above, proved in conformity with those of the last named authors. The equilibrium between copper, cupric and cuprous salts in presence of hydrochloric acid is represented by two equations:

$$\overset{\circ}{Cu} + \overset{\cdot\cdot}{Cu} \rightleftharpoons 2\,\dot{Cu} \qquad (1)$$

$$\dot{Cu} + 2\,\acute{Cl} \rightleftharpoons Cu\,\acute{Cl}_2 \qquad (2)$$

Bodländer and Storbeck determined the values of the constants $k_1 = (\overset{\cdot\cdot}{Cu})/(\dot{Cu})^2$ and $k_2 = (Cu\acute{Cl}_2)/(\dot{Cu})(\acute{Cl})^2$ as 1.4×10^4 and 4×10^4, respectively, concentrations being in mols per litre.

The second part of the investigation had for its object the determination of the concentration at the anode during the electrolytic experiments, so that the values of k_1 and k_2 might be calculated from these and compared with those obtained from the equilibrium experiment. Fig. 1 is a diagram of the electrolytic cell used. It consisted of two porous cylinders, P_1 and P_2, between the ebonite discs, E E, two concentric glass cylinders, L and M, also held between ebonite discs, and a rotating copper anode, A, making contact with a shaft and holder, H. To prevent liquid from entering within the anode tube, two ebonite plugs (the lower of these having a glass Tip, T) were provided with threaded holes, so that they could be tightened against the copper, as shown in the diagram. The tube could therefore be taken off the plugs and weighed. Its area was about 40 square centimetres. A rubber tube, with stopper, S, fitted over the upper plug. The electrolyte entering B passed between the two porous cylinders, through holes in the center disc, E, and the glass cylinder, M, and up and around the anode, leaving by means of the exit tube, D. The cathode consisted of a platinum gauze, C, attached around the discs E. The different parts were cemented together. Cork wedges between the discs and the glass container, F, prevented any lateral motion of the discs when the anode was set rotating.

Since hydrochloric acid containing air in solution dissolves

[3] G. Bodländer and O. Storbeck, Zeit. f. Anorg. Chem., 31, 1. 458.

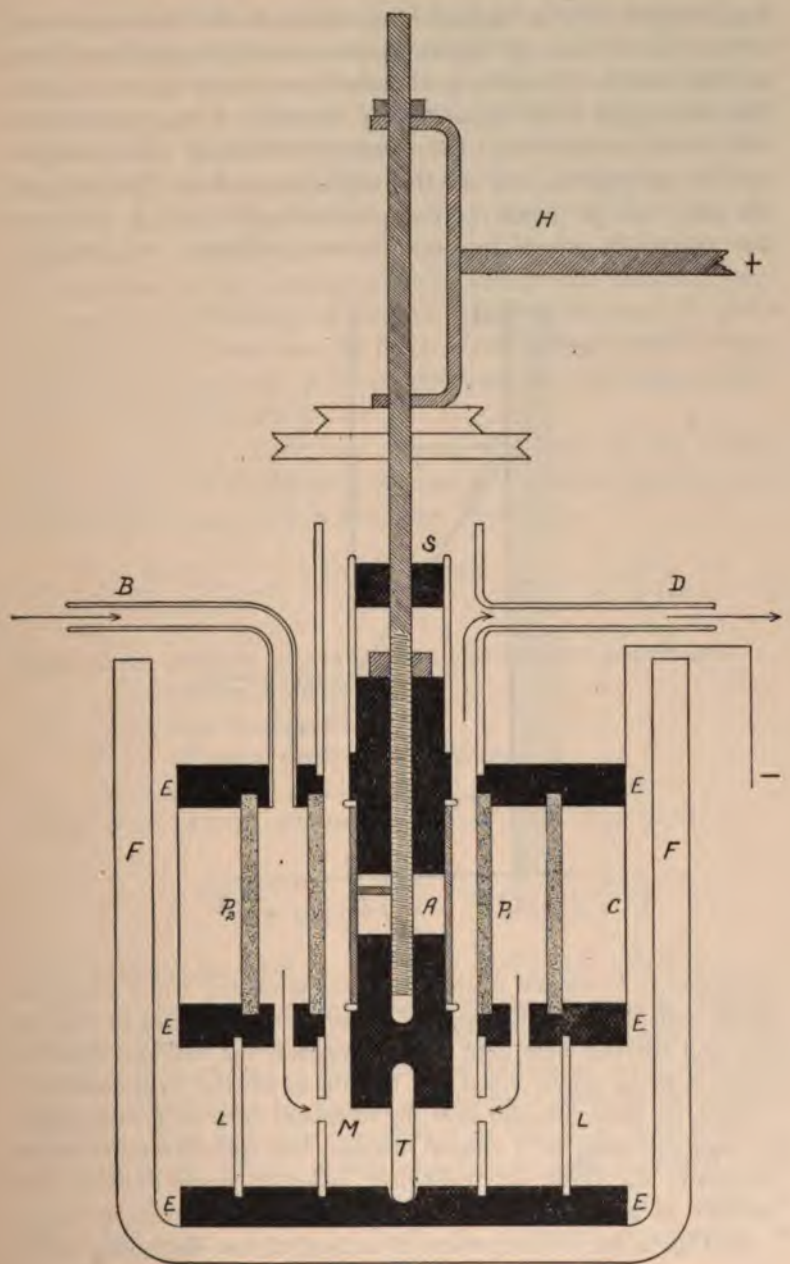

FIG. 1.

copper even without current, the solution to be electrolyzed was always freed from air by exhaustion, and then saturated with carbon dioxide. Blank experiments showed that in such a solution the copper dissolved only very slightly. A large bottle filled with stock solution was permanently connected with a carbon dioxide generator, and as the solution ran out into the cell, the gas took its place. After circulating through a cell once, the electrolyte passed into a measuring cylinder, and was then

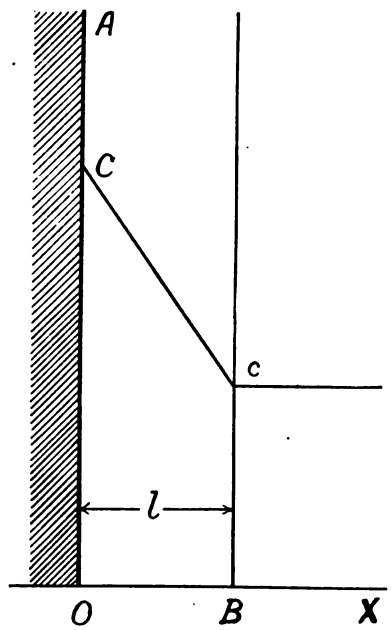

FIG. 2.

discarded. A copper coulometer and ammeter were placed in series with the cell. During the experiment, the rates of circulation and stirring were kept nearly constant, the average speed of rotation being about 1,500 per minute in all the experiments.

Now we shall consider how, by means of such an arrangement, we can calculate, in a simple manner, the concentrations at the electrode, for these are evidently different from those in the solution at a distance from the electrode.

In Fig. 2, let OA represent a section of the electrode, whose

area is S. Let OX represent the distance from the electrode. It has been shown by Nernst and Brunner that in a rapidly stirred solution the diffusion is limited to a very thin layer close to the electrode, the thickness L decreasing with increasing rate of rotation. Outside this layer, the solution is of uniform composition. The concentrations of $\ddot{C}u$, for example, at the electrode and in the solution are represented by OC and Bc, respectively. Owing to the circulation of the electrolyte, the concentration in the solution rapidly attains the constant value Bc, and the distribution of concentrations in the layer is given by the line Cc. Now since all the concentrations remain constant during the electrolysis, it is evident that the following relation exists between OC and Bc:

The amount of cupric ion entering the layer in any time is equal to the amount diffusing out into the solution, together with the amount transported in the same time, Or

$$\frac{a\,i\,t}{2 \times 96540} = \frac{D\,S\,t\,(C-c)}{L} + \frac{n\,i\,t}{2 \times 96540}$$

where a = fraction of current used to produce cupric ion,
i = current in amperes,
t = time in seconds,
D = diffusion constant in cms/sec.,
n = transport number of ion in the solution.

Since c = ait/2 × 96,540 V where V = volume in cc.,

$$C = \frac{a\,i\,t}{2 \times 96540}\left(\frac{1}{V} + \frac{L\,(1-n)}{D\,S\,t}\right)$$

Similar equations hold for the other ions in the solution.

The thickness of the layer was determined by two different methods, and both gave approximately the same result. It was about 6×10^{-4} cms. The diffusion constants were calculated from the mobilities by means of Nernst's formula as modified by Bose. The fall in concentration in the layer was found to be very large. Thus, in one experiment with N/200HCl, the concentration of $\ddot{C}u$ at the electrode was 0.8×10^{-3}, while in the solution it was 0.3×10^{-3}. In different experiments, in

which the concentrations of HCl, $\ddot{Cu}$, $\dot{Cu}$ and $CuCl_2'$ varied, the value of the constant $k_1 = (\ddot{Cu})/(\dot{Cu})^2$ was nevertheless very fair, being about 0.3×10^4, instead of 1.4×10^4, as determined by Bodländer and Storbeck.

However, considering the various assumptions on which these calculations have been made, I consider the agreement fair. Experiments are still in progress by which I hope to obtain more accurate results, but the data so far obtained seem to emphasize this point: By the assumption of instantaneous equilibrium at the boundary between anode and solution, the apparently erratic results are reduced to agreement with Faraday's Law.

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UNIVERSITY OF TORONTO STUDIES

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PAPERS FROM THE CHEMICAL LABORATORIES

No. 77: THE EFFECT OF FERRIC SALTS ON THE RATE OF OXIDATION OF FERROUS SALTS, BY W. F. GREEN

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THE EFFECT OF FERRIC SALTS ON THE RATE OF OXIDATION OF FERROUS SALTS, AND ON THE CATALYTIC ACTION OF THE LATTER.

BY W. F. GREEN

Experiments carried out in this laboratory by Miss C. C. Benson in 1902–1904[1] showed that the oxidation of ferrous sulphate by chromic acid is much retarded by the presence of ferric salts, and that the catalytic action of ferrous salts on the oxidation of iodides by chromic acid is likewise greatly diminished by the same reagent.

In the hope of throwing light on this remarkable case of negative catalysis, I have studied the effect of ferric salts on the rate of oxidation of ferrous salts by chloric acid and by oxygen and on the rate of oxidation of iodides by chloric acid and by bromic acid in the presence of ferrous salts.

I. Oxidation of ferrous chloride by chloric acid

The rate of this reaction has been studied by Noyes;[2] no effect of the ferric salt on the rate is apparent in his results; direct measurements, however, were undertaken to make sure.

The measurements were carried out in stoppered bottles, under carbon dioxide, in a thermostat at 30° C. as described by Noyes. The volume of the reacting solution was 250 cc in each case. The solution of ferrous chloride, free of ferric, contained 0.4148 equivalent (52.60 grams $FeCl_2$) per liter; the potassium chlorate 0.500 equivalent (10.21 grams $KClO_3$) per liter; while the hydrochloric acid was 1.022 normal, and the permanganate used in titration was 0.122 normal.

The reagents were present in almost equivalent quantities, and from the results of the measurements the "constant" K of the kinetic equation $dx/dt = K(A - x)^3$ was

[1] Jour. Phys. Chem., 7, 1, 356 (1903).
[2] Zeit. phys. Chem., 22, 210 (1897).

calculated, in which A represents the geometrical mean of the numbers of equivalents of the three reagents present at the moment $t = 0$. In order to avoid "initial disturbances," the time of the first analysis was taken as zero for t and for x, the composition of the solution at that moment being calculated from the known quantities of the stock solutions used in making it up, and the result of the first analysis.

At the head of each table is given the number of equivalents of each reagent per liter at $t = 0$; under t the time from the first titration in minutes; under "titration" the number of cubic centimeters of permanganate used in titrating 25 cc of the reacting solution; under D the differences from the last column; under $x = \frac{0.122\ D}{25}$ the equivalents of ferrous salt oxidized per liter; and under K the constant calculated as explained above.

The reacting solution of Table 1 contained initially only the trace of ferric salt formed in the two minutes which elapsed between the time of mixing and the first titration. The solutions of Table 2 contained 20 grams ferric ammonium alum per liter; that of Table 3, 40 grams of the alum; and that of Table 4, 64 grams. The values of K are practically the same for all; in other words the ferric salt exerts no appreciable retarding influence on the rate.

TABLE 1

$Fe'' = 0.1169$, $Chl = 0.0925$, $Ac = 0.0947$, $(A = 0.1008)$, $Fe''' = 0$

Number	T	Titration	D	x	K
1	0	23.95	—	—	—
2	13	19.10	4.85	0.0237	0.054
3	30	15.90	8.05	0.0393	0.056
4	45	14.22	9.73	0.0475	0.056
5	60	13.05	10.90	0.0532	0.058
6	90	11.45	12.50	0.0610	0.060

TABLE 2

Fe'' = 0.1179, Chl = 0.0935, Ac = 0.0957, (A = 0.1018), Fe''' = 0.0416

Number	T	Titration	D	x	K
1	0	24.15	—	—	—
2	12	20.10	4.05	0.0198	0.045
3	30	16.65	7.50	0.0366	0.048
4	45	14.77	9.38	0.0458	0.051
5	60	13.48	10.67	0.0521	0.053
6	90	11.80	12.35	0.0603	0.056

TABLE 3

Fe'' = 0.1152, Chl = 0.0908, Ac = 0.0930, (A = 0.0991), Fe''' = 0.0832

Number	T	Titration	D	x	K
1	0	23.60	—	—	—
2	31	16.15	7.45	0.0364	0 048
3	60	13.50	10.10	0.0493	0.049
4	93	11.50	12.10	0.0591	0.057

TABLE 4

Fe'' = 0.1145, Chl = 0.0901, Ac = 0.0923, (A = 0.0984), Fe''' = 0.1330

Number	T	Titration	D	x	K
1	0	23.45	—	—	—
2	31	15.85	7.60	0.0370	0.051
3	60	13.00	10.45	0.0510	0.055
4	93	11.00	12.45	0.0608	0.063

II. Oxidation of ferrous sulphate by oxygen

This reaction was studied here by Mr. J. W. McBain in 1901.[1] I used the method of working and of analysis described by him, and his apparatus for the preparation and storage of the solution of oxygen, which was saturated with the gas at 15.5° C and 758 mm barometer. The ferrous sulphate solution was freed from ferric salt by barium carbonate

[1] Jour. Phys. Chem., 5, 623 (1901).

as described by Miss Benson;[1] it was kept under carbon dioxide and gave no red color with potassium sulphocyanate.

In every case the reacting solution contained 200 cc of 1.05 normal sulphuric acid[2] and 200 cc oxygen water per liter; the amounts of ferrous sulphate and ferric chloride in mols per liter are given at the head of each table. All experiments were carried out at 30° C.

The standard solution used for comparison in the colorimeter was made up fresh for each experiment, by mixing a solution containing 0.0966 gram $FeCl_3$ per liter of normal sulphuric acid, with its own volume of an aqueous solution of ammonium sulphocyanate containing 47.5 grams of the salt per liter.

In making an analysis, 25 cc of the reacting mixture were added to 12.5 cc of the ammonium sulphocyanate, and to this (except in the case of Table 5) 50 cc of water were added; 15 cc of the colored solution so prepared were placed in the colorimeter tube. Twenty-five cc 0.00459 normal ferric chloride thus treated matched 14 mm of the standard color if the 50 cc water had been added, 52.5 mm if it had not. In Tables 5 and 6 each analysis was made from the contents of a separate stoppered bottle; in Tables 7 and 8 samples were pipetted from a larger quantity.

In Tables 5 and 6 the differences are entered under "amount oxidized" in the last column. Their equality shows that the ferric salt has no influence on the rate. In the experiments of Tables 7*a* and 8*a*, immediately before the second analysis, ferric chloride was added to the reacting solution in such quantity that the amount added per liter was equal to the amount added per liter to the solutions of 7*b* and 8*b* respectively at the beginning of the experiment. The agreement between the results of the last three analyses in Tables 7*a* and *b* and 8*a* and *b* respectively shows that the presence of ferric chloride during the first seventeen hours of the reaction had no effect on the rate.

[1] Jour. Phys. Chem., 7, 5 (1903).

[2] Except Table 5B where 250 cc acid was used.

TABLE 5

5(*a*) $Fe''' = 0$, $Fe'' = 0.229$					5(*b*) $Fe''' = 0.0119$, $Fe'' = 0.229$				
No.	Time Hrs.	Min.	Reading in mm.	Amount oxidized	No.	Time Hrs.	Min.	Reading in mm.	Amount oxidized
1	0	07	5.0	—	1	0	07	7.5	—
2	3	02	23.5	18.5	2	3	02	27.5	20.0
3	5	33	35.5	30.5	3	5	33	36.5	29.0
4	23	25	60.0	55.0	4	23	25	59.5	52.0
5	28	06	64.0	59.0	5	28	06	68.0	60.5

TABLE 6

6(*a*) $Fe''' = 0$, $Fe'' = 0.2384$					6(*b*) $Fe''' = 0.0119$, $Fe'' = 0.2384$				
No.	Time Hrs.	Min.	Reading in mm.	Amount oxidized	No.	Time Hrs.	Min.	Reading in mm.	Amount oxidized
1	0	08	0.0	—	1	0	07	12.0	—
2	1	50	5.0	5.0	2	1	50	16.0	4.0
3	20	00	11.0	11.0	3	20	00	21.0	9.0
4	70	25	11.5	11.5	4	70	25	23.5	11.5

TABLE 7

7(*a*) No. 1, $Fe''' = 0$; No. 2, $Fe''' = 0.0238$; $Fe'' = 0.2384$				7(*b*) $Fe''' = 0.0238$, $Fe'' = 0.2384$			
No.	Time Hrs.	Min.	Reading in mm.	No.	Time Hrs.	Min.	Reading in mm.
1	0	03	0.0	1	0	06	17.0
2	17	30	34.5	2	17	35	34.5
3	22	54	48.5	3	22	54	48.0
4	43	15	88.0	4	43	15	89.0

TABLE 8

8(a) No. 1, Fe''' = 0; No. 2, Fe''' = 0.0238; Fe'' = 0.1907				8(b) Fe''' = 0.0238, Fe'' = 0.1907			
No.	Time Hrs.	Min.	Reading in mm.	No.	Time Hrs.	Min.	Reading in mm.
1	0	03	0.0	1	0	04	20.0
2	17	50	41.5	2	17	50	42.0
3	22	49	49.5	3	22	49	51.0
4	43	18	68.0	4	43	18	68.0

III. Catalysis of the reaction between chloric and hydriodic acids

This reaction has been studied here by Mr. W. C. Bray in 1902–3.[1]

He found that addition of a little ferrous salt greatly accelerated the rate. I have measured the effect of ferrous and ferric salts on the rate, and also the effect of ferric salt on the catalysis by ferrous.

In my experiments I followed Bray, working in stoppered bottles under carbon dioxide at 30° C. In every case the total volume of the reacting solution was 250 cc, containing initially 50 cc of normal hydrochloric acid, 50 cc of normal potassium iodide, and 10 cc half-normal potassium chlorate (p. 389); the iron is given at the head of the tables, the unit being 55.9 grams iron (ferrous or ferric) per liter. Fifty cc were removed for analysis, and titrated with hundredth-normal thiosulphate. In calculating the constant $K = 1/t \log_{10} (A/A - x)$ the time of the first titration, made within one minute of adding the iodide, was taken as $t = 0$; the amount of this titration was subtracted from all subsequent readings before entering them in the tables, and from 50.00 to give the value of A.

The results show that the reaction is greatly accelerated by both ferrous and ferric salts; that the acceleration is practically equal for equal amounts of iron independent of its

[1] Jour. Phys. Chem., 7, 92 (1903).

state of oxidation; and that in solutions containing both ferrous and ferric salt, the effects of the two are additive. The presence of ferrous salt in the solution of Table 12, after standing for twenty-four hours, was shown by potassium ferricyanide.

TABLES 9 AND 10

9. Fe = 0,				10 Fe″ = 0.0005,			
No.	t	$A-x$	K	No.	t	$A-x$	K
1	0.0	50.0	—	1	0.0	49.75	0 0
2	35.0	0.1	0.000034	2	35.0	48.00	0.00045
3	97.0	0.3	0.000018	3	95.0	45.00	0.00046
4	1200.0	1.52	0.000011	4	116.0	44.20	0.00044
				5	1197.0	13.80	0.00046

TABLES 11 AND 12

11 Fe‴ = 0.0005				12 Fe″ = 0 0005, Fe⁗ = 0 0005			
No.	t	$A-x$	K	No.	t	$A-x$	K
1	0.0	44.30	—	1	0.0	44.4	—
2	30.0	43.00	0.00043	2	15.0	43.0	0 00093
3	77.0	40.30	0.00053	3	30.0	41.5	0.00098
4	90.0	39.65	0.00054	4	45.0	40.2	0.00096
5	1159.0	7.15	0 00060	5	62.0	38.9	0.00091
				6	92.0	36.6	0.00091
				7	105.0	35.3	0.00095
				8	150.0	33.2	0.00085

TABLES 13 AND 14

13 Fe″ = 0.001				14 Fe‴ = 0.001			
No.	t	$A-x$	K	No.	t	$A-x$	K
1	0.0	48.40	—	1	0.0	44.50	—
2	15.0	46.95	0.00087	2	15 0	43.10	0.00093
3	30.0	45.40	0.00092	3	30.0	41.70	0.00094
4	45.0	44.00	0.00092	4	45.0	40.15	0.00100
5	62.0	42.40	0.00093	5	62.0	38 65	0.00099
6	92.0	39 90	0 00091	6	92.0	36.10	0.00099
7	105.0	38.90	0 00090	7	105,0	35.00	0.00099
8	150.0	35.45	0.00090	8	150.0	31.45	0.00101

IV. Catalysis of the reaction between bromic and hydriodic acids

This reaction has been studied here by Mr. Clark[1] in 1904–5, and I followed his method of working, mixing the iron salts with the iodide and acid before adding the bromate.

In each experiment the total volume of the reacting solution was 250 cc, containing 10 cc decinormal potassium iodide, 20 cc decinormal hydrochloric acid, and 10 cc decinormal potassium bromate (one sixtieth formula weight per liter); the iron present is given at the head of each table in formula-weights Fe (ferrous or ferric) per liter. In each experiment the temperature was 30° C, and the duration of the reaction thirty minutes. The numbers in the tables give the volume (cubic centimeters) of hundredth-normal arsenite oxidized in two or four duplicate experiments, the total reduction of the bromate corresponding to 100 cc arsenite.

Except where the presence of large amounts of ferric salt interfere with the titration, the results of the duplicates are in fair agreement; they show that, as in the case of chloric acid, equal weights of ferrous and ferric iron have the same effect on the rate, and that in mixtures as well the acceleration depends only on the total amount of iron present.

TABLE 15

$t = 30$. Readings in cc. of n/100 sodium arsenite

No.	Fe = 0	Fe'' = 0.0002 per liter	Fe''' = 0.0001 per liter	Fe'' = 0.0004 per liter	Fe''' = 0.0002 per liter	Fe'' = 0.0002 Fe''' = 0.0001 per liter
1	4.86	8.92	8.86	11.67	9.80	10.04
2	4.95	8.94	8.83	11.92	11.32	10.83
3	—	—	—	11.65	10.94	10.45
4	—	—	—	11.89	10.24	10.44

Conclusion

The oxidation of ferrous salt by chloric acid, and by oxygen, is not retarded by addition of ferric salt; neither is the catalytic action of ferrous salt on the oxidation of hy-

[1] Jour. Phys. Chem., 10, 679 (1906).

driodic acid by chloric or bromic acids. The negative catalysis which ferric salts exert on the oxidation of ferrous salts by chromic acid, and on the liberation of iodine in solutions containing ferrous salt, chromic and hydriodic acids, thus stands alone.

Ferric salt is without effect on the rate of oxidation of ferrous salt by chloric acid and by oxygen. Both ferrous and ferric salts accelerate the liberation of iodine in solutions containing chloric or bromic acid and hydrogen iodide, the rate depending merely on the amount of iron present, and not on its state of oxidation.

These measurements were carried out at the suggestion of Prof. W. Lash Miller in the winter of 1904–5.

The University of Toronto,
Chemical Laboratory,
March, 1908.

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No. 78: LOSS OF CARBON DURING SOLUTION OF STEEL IN POTASSIUM CUPRIC CHLORIDE, BY E. P. MOORE AND J. W. BAIN

(REPRINTED FROM THE JOURNAL OF THE SOCIETY OF CHEMICAL INDUSTRY, VOL. XXVII)

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Canadian Section.

Meeting held at Toronto on Thursday, May 16, 1908.

PROF. W. H. ELLIS IN THE CHAIR.

LOSS OF CARBON DURING SOLUTION OF STEEL IN POTASSIUM CUPRIC CHLORIDE.

BY E. P. MOORE AND J. W. BAIN.

There has been much uncertainty as to whether carbon is lost by the evolution of gaseous hydrocarbons during the solution of steel in acid potassium cupric chloride solution when this method is used for the determination of carbon in that metal. Dillner(1) remarks, "As is well known and as has been pointed out on several occasions by various authorities, there is always an evolution of hydrocarbon gases when steel dissolves in copper chloride, which escape"; accounting in this way for the lower results obtained from the indirect processes. He also refers to some observations made by Ledebur(2), but unfortunately the publication was inaccessible. Arnold (3) states that he has seen distinctly bubbles rising through the liquid during the solution of steel in copper chloride.

The problem has hitherto been attacked from the following standpoint. Samples of steel are dissolved in various solvents of various concentrations and the carbon estimated as usual. The highest percentage obtained is selected as a standard and the discrepancies between this and the other results are ascribed to losses during solution. True, these results are confirmed by determinations made by the volatilisation of the iron by chlorine or by direct combustion, but even in these cases the uncertainty of a numerical difference between two results, each burdened with experimental errors, is obvious. For these reasons it appeared to be desirable to determine, by a direct process if possible, whether any carbon was lost during the solution of iron or steel in the solvent so commonly used—potassium cupric chloride.

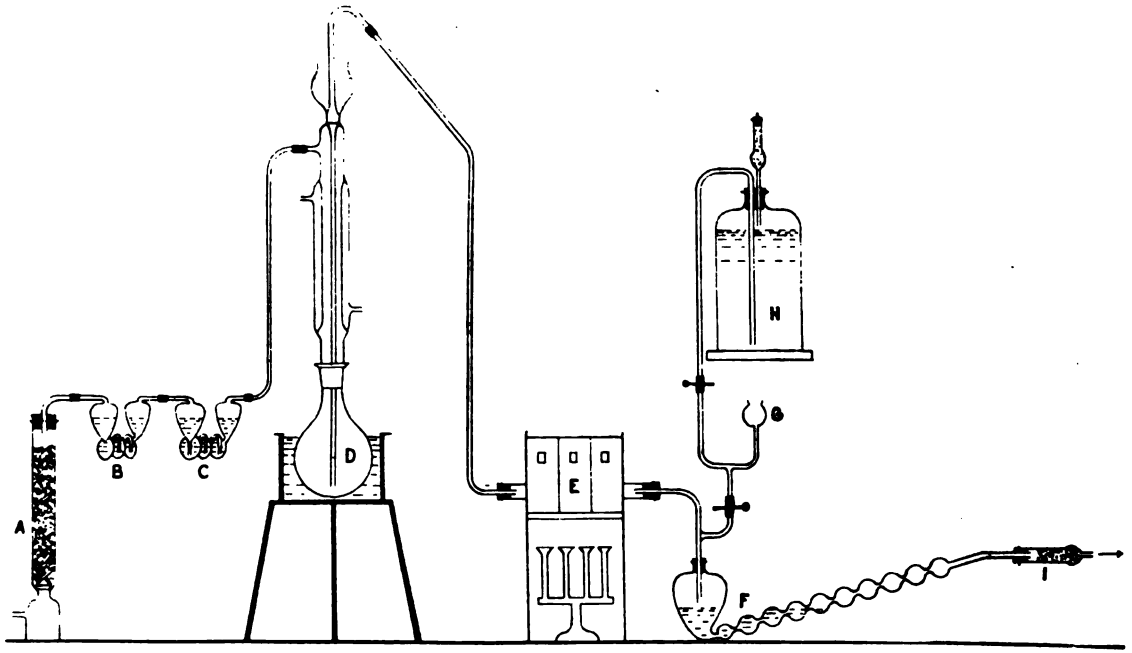
The following apparatus was used (see figure):—A, A drying tower filled with potassium hydroxide in sticks. B, An absorption bulb filled with potassium hydroxide solution. C, An absorption bulb filled with barium hydroxide solution. D, A Rheindorf(4) flask for estimation of carbon, immersed in a water bath maintained at a temperature of 65° C. E, A piece of combustion tubing filled with cupric oxide, heated to redness in a small gas furnace. F, A ten bulb absorption apparatus charged with barium hydroxide. G, A small thistle

tube sealed to a glass T as shown. H, A stock bottle containing barium hydroxide. I, A guard tube filled with soda-lime. The introduction of barium hydroxide into the absorption bulb is the only feature which calls for remark. A current of air free from carbon dioxide having been drawn through the bulb, F, for some time, a suitable quantity of barium hydroxide solution was siphoned over, being clarified in transit by passing through a filter of ignited asbestos (not shown). In the first experiments a slight precipitate formed on the inner surface of the delivery tube which protrudes into the bulb, F; by pouring into the funnel, G, a small quantity of recently-boiled distilled water and allowing it to wash down, it was found that this could be entirely avoided.

The flask, D, was charged with a solution of potassium cupric chloride made by dissolving 300 grms. of the salt in 1 litre of water and adding 75 c.c. of concentrated hydrochloric acid. Blank tests were made by placing in the flask, D, the quantity of potassium cupric chloride solution usually employed, and after aspirating for some time to clear the apparatus of carbon dioxide, filling the bulb, F, with barium hydroxide solution, and proceeding to heat the flask, D, to 65° C. After aspirating for two hours, in no case was there more than a very faint cloud of barium carbonate to be observed in the tube, F; efforts were made to collect and weigh this precipitate, but without success. Three grms. of steel were then placed in the solution flask, 200 c.c. of potassium cupric chloride solution added, and the water bath maintained at a temperature of 65° C.; air was also slowly aspirated through the apparatus, the cupric oxide having been previously brought to red heat. When the steel had dissolved completely, the ten bulb tube was removed, and a stopper carrying a soda-lime tube placed immediately in the larger end, while the other opening was connected by rubber tubing to the glass tube in the cork of a filtering funnel. The barium carbonate was transferred as completely as possible to the filter and washed with recently-boiled distilled water; the absorption tube and the filter were then treated with dilute hydrochloric acid, the asbestos filtered off, and the barium precipitated as sulphate and weighed.

Two samples of steel were employed; the one containing 0·653 per cent. of carbon, the other 1·18 per cent. Four determinations were made on each of these, 3 grms. being used in each case; the results are expressed as grms. of carbon escaping from the flask.

	0·653 per cent. Steel.	1·18 per cent. Steel.
	grm.	grm.
	0·00176	0·00115
	0·00112	0·00121
	0·00142	0·00100
	0·00159	0·00103
Mean	0·00147	0·00110
Loss on 1 grm.	0·0005	0·0004


A
B
C
D
E
F
G
H
I

In the case, therefore, of the 0·653 per cent. steel, a quantity of carbon corresponding to 0·05 per cent. has been lost during solution, making the true percentage 0·703; with the other the true percentage will be 1·22.

These losses are comparatively large, although not much greater than some of the discrepancies between the results obtained by various members of the International Committee. In view of the difficulties in manipulation the authors do not profess that their figures represent the actual loss, but they believe that they have proved that a loss does take place under the conditions given above, and also that the amount approximates fairly closely to the figures given.

---

(1) J. Iron and Steel Inst., 66, 255.

(2) Verein zur Beförderung der Gewerbfleisses, Vols. 6, 7.

(3) Steel Works Analysis, 2nd ed., p. 29.

(4) Zeits. angew. Chem., 1904, 467.

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No. 79: THE INDUCTION BY FERROUS SALTS OF THE REACTION BETWEEN CHROMIC AND HYDRIODIC ACIDS,

BY ROSS A. GORTNER

(REPRINTED FROM THE JOURNAL OF PHYSICAL CHEMISTRY, VOL. XII).

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THE INDUCTION BY FERROUS SALTS OF THE REACTION BETWEEN CHROMIC AND HYDRIODIC ACIDS

BY ROSS A. GORTNER

Reprinted from the Journal of Physical Chemistry, Vol. 12, No. 8, November, p. 630 (1908)

THE INDUCTION BY FERROUS SALTS OF THE REACTION BETWEEN CHROMIC AND HYDRIODIC ACIDS.

BY ROSS A. GORTNER

The reaction between chromic acid, ferrous salts and hydriodic acid, studied here some years ago by Miss C. C. Benson,[1] presents many points of interest which invite further investigation: the great influence of the acid concentration on the rate, the retarding action of ferric salts, and the observation that less iodine is liberated per second at 30° C than at 0° C, are all most unusual. Mr. Green's work on catalysis by ferric salts, recently published,[2] which shows that nothing similar to the retardation observed by Miss Benson is to be met with in the behavior of reactions otherwise closely analogous, adds interest to this exceptional case.

My own measurements, described in the present paper, show that the lessened retardation observed when "aged" portions of the oxidation product were added to the reaction mixture is quantitatively ascribable to the hydrolysis of the ferric salts, and that colloids and colloidal ferric hydrate in particular have but little effect on the rate. Sulphuric acid may be replaced by hydrochloric acid without changing the general nature of the results, but the addition of fluorides, chlorides or bromides retards the liberation of iodine and accelerates the oxidation of the ferrous salt. This observation may be accounted for very naturally by an explanation in keeping with Miss Benson's Ferroiodion theory; it may therefore be regarded as furnishing independent evidence in support of the latter. Miss Benson's observation that the rate of liberation of iodine at 30° C is less than at 0° C, is confirmed and supplemented by experiments which show that the rate of oxidation of the iron is greater at the higher temperature.

[1] Jour. Phys. Chem., 7, 1 (1903); 7, 356 (1903); 8, 116 (1904).

[2] *Ibid.*, 12, 389 (1908).

Method of working and of recording the results

In the composition of the solutions, in the methods of manipulation, and in the temperatures worked at, I closely followed the details described by Miss Benson;[1] and after a little practice found that on repeating her experiments I obtained identical results. In tabulating the measurements, also, the symbols and arrangement described on page 359 of the paper referred to have been adopted;[2] for convenience it may be repeated here that the numbers after the symbols Ac, Cr, KI, Fe, are very closely proportional to the number of equivalents of the various reagents present in the reacting solution—one formula-weight of bichromate being equivalent to seven of sulphuric acid and to six of ferrous sulphate or potassium iodide.

To facilitate reference, my tables and experiments are numbered consecutively with those of Miss Benson's last paper.

Effect of chlorides, bromides, and fluorides on the rates

When hydrochloric acid is substituted for sulphuric acid (Table XXXVI) *the rate of liberation of iodine is somewhat reduced*, but still remains proportional to a high power of the concentration of the acid. The retardation cannot be ascribed to the action of the ferric salt, for, as is shown on page 636, ferric chloride and ferric sulphate have the same effect on the rate; it is explained by the experiments of Table XXXVII, which show that addition of sodium chloride, potassium bromide, or potassium fluoride reduces the rate of liberation of iodine; potassium sulphate is without effect.

---

[1] Ac 10 represents 10 cc of 0.059 F sulphuric acid (*i.e.*, acid containing 0.059 formula weights H_2SO_4 per litre); Cr 10, 10 cc of 0.0083 F potassium bichromate (including unreduced bichromate, if any, in the oxidation product); KI 10, 10 cc of 0.0479 F potassium iodide; Fe 1, 10 cc of 0.05 F ferrous sulphate; Ox 5, the product of oxidation of 5 cc of 0.05 F ferrous sulphate. The duration of the reaction in minutes is entered in the tables under Θ; the number of cc of N/100 sodium arsenite equivalent to the iodine liberated, under As; and the number of units of ferrous salt oxidized, under x, 10 cc 0.05 F ferrous salt being taken as the unit. As = $5y$.

[2] Jour. Phys. Chem., 7, 357 (1903).

The measurements of Table XXXVIII[1] show that *the rate of oxidation of iron is increased* by addition of fluoride. These observations may be explained very naturally by assuming that the halogen and the ferro-ion unite to form a complex FeF′ (analogous to the ferroiodion FeI′ of Miss Benson's hypothesis);[2] this substance on oxidation would yield ferric salt but no iodine, the induction factor should therefore fall off with increase in the concentration of the fluoride, as observed. To account for the increased rate of oxidation of the iron, it is only necessary to assume that the complex FeF′ is more rapidly oxidized than Fe″ (or FeI′).

The effect of colloids on the rate

The fact that under certain circumstances ferric hydrate can exist in the colloidal form, suggested experiments with other colloids. Agar-agar in one-tenth percent solution has no effect. Egg albumen, two-tenths percent solution, retards the oxidation, but this is probably due to its action as a weak base,[3] the retardation being proportional to the amount of albumen used. "Dialyzed iron" (colloidal ferric hydrate) retards a little, but nothing like as much as the same quantity of ferric sulphate or chloride—see Table XXXIX.

On the whole, therefore, the colloids experimented with have no retarding action to be compared with that of the ferric salts.

Diminished retardation by "aged" ox. prod.

When the product of oxidation of ferrous sulphate by chromic acid (ox prod) is allowed to stand, it gradually de-

[1] The values of x in this and other tables of this paper are obtained by interpolation from the data of part B of the table, as explained in this Journal, 7, pp. 3 and 364 (1903).

[2] Undissociated FeI_2, FeF_2, etc., or the corresponding acids might be assumed; the type of the reaction however is fixed by Miss Benson's measurements. See Jour. Phys. Chem., 11, 9 (1907). W. L. M.

[3] Ber. chem. Ges. Berlin, 28, Ref. 858 (1895).

posits a yellow brown precipitate and its retarding power is lessened.[1] Similar changes in solutions of ferric chloride have been studied by Goodwin,[2] who showed by conductivity measurements that the "ageing" of the solutions was due to hydrolysis. In solutions of the strength of my "ox prod" this hydrolysis is accompanied by the formation of a precipitate, so that the concentration of the ferric salt is reduced, and that of the acid is increased—both changes tending to accelerate the liberation of iodine. The experiments of Tables XL and XLI show that the increased rate actually observed when "aged" ox prod is used can be completely accounted for if these changes in acidity and ferric concentration are taken into consideration.

In these experiments, three ferric solutions were used. The first was that employed in most of my work at 0° and is referred to in the tables under the title "Ox": it was prepared fresh by making up 200 cc acid, 600 cc bichromate and 20 cc ferrous sulphate (the undiluted solutions were used) to two liters; 50 cc contained the oxidation product of 5 cc decinormal ferrous sulphate, and in addition, 10 cc F/120 bichromate unreduced,[3] but no free acid. The second was prepared from the first by boiling for about half a minute, filtering hot and cooling; the third was obtained by allowing some of the first to stand 64 days at room temperature and filtering. The ferric salt in each of these three was determined volumetrically. by stannous chloride and bichromate; the bichromate was determined by titration with ferrous sulphate; and the acid by adding excess of volumetric potassium hydrate, and titrating back with sulphuric acid (without filtration) using methyl orange as indicator. The last determination gave both the free acid and that combined with the ferric salt; the latter was calculated from the ferric determination and subtracted. Fifty cc of each of the three preparations contained respectively:

[1] Jour. Phys. Chem., 7, 362 and Table 15 pp. 384.
[2] Zeit. phys. Chem., 21, 1 (1896).
[3] Jour. Phys. Chem., 7, 359 (1903).

	I	II	III
Ferric salt	5.0	1.0	2.87
Bichromate	10.0	10.0	10.0
Free acid	0.0	5.0	2.6

in the units defined on page 633.

In Table XL the volume and the distinguishing number of the ferric solution used in each experiment is given under Ox, also the ferric salt and the free acid contained in it ("Ac from Hydrol"); under "acid added" is entered the amount of acid from the stock solution; the "total acid" is obtained by adding the last two.

Hydrolysis of the ferric solution (ox prod) can be completely prevented by making it up with excess of acid instead of with excess of bichromate; and further experiments (Table XLI) show that an acid solution of ferric chloride may be substituted without affecting the rates. The solutions used contained, in 50 cc:

	IV	V
Ferric (sulphate)	5.0	0.0
Ferric (chloride)	0.0	5.0
Free acid	10.0	10.0
Bichromate	0.0	0.0

Experiments at 30.5° C

Miss Benson has shown that by titrating as directed on page 357 of her paper, the amount of iodine liberated by the reaction may be determined accurately if both reaction and titration are carried out at 0° C; experiments of my own confirm this conclusion. At 30° C, however, owing no doubt to the fading of the blue color of iodide of starch at high temperatures, a considerable excess of iodine—from 0.6 to 0.8 cc N/100 iodine in the 700 cc of solution—is necessary to produce the permanent tint taken as end point. When any arsenite was required in the "blank" experiment (without ferrous salt) the same correction for the end point would

apply there; and in these cases the net arsenite (after subtracting the "blank") would be free from error. When "As = 0" in the blank experiment however, *i. e.* when the iodine liberated in the blank experiment was less than enough to give the blue with starch, the numbers are too low. This is the case with most of Miss Benson's measurements from Table XXIV onward. I have consequently repeated the determinations at 30° C; the results are contained in Tables XLV to XLIX. While confirming Miss Benson's conclusions as to the effect of the concentrations of the various reagents on the rate of liberation of iodine, they show that the rate of oxidation of the iron in the solution is much more rapid at the higher temperature, and that in many cases all the iron is oxidized within two minutes; this result was checked by addition of potassium ferricyanide.

The correction for the end point (which in all the tables has been added to the observed numbers before entering them under "As") is given at the head of each table; it varies slightly from case to case, and was obtained as follows: The amounts of acid, bichromate, and "ox. prod." indicated at the head of the table were mixed at 30° C with water and 10 cc of a saturated solution of iodine in water, the ferrous sulphate was then added with enough water to bring the whole to a volume of 700 cc; one minute later ammonium bicarbonate was added, then 5 cc normal potassium iodide, and starch, and then N/100 arsenite to the "end point." In order to find the arsenite equivalent of the iodine employed, 10 cc of the same iodine solution was then added, and arsenite to the end point again; in every case 1.90 cc arsenite was required. Table XLII shows that the "correction" does not depend on the length of time the reacting solution remained in the bath, loss of iodine from evaporation is therefore not to be feared.

The induction factor at 0° and at 30°

Miss Benson has shown[1] that the induction factor—or

[1] Loc. cit., page 369.

the number of equivalents of iodine liberated per equivalent of iron oxidized—varies, at 0° C, from 1.2 to 1.8. To make the evidence for this as clear as possible, I have calculated the induction factor, *viz.*, the fraction y/x, from the data of her Table XVII, and present the results in Table XLIII. At 30° the induction factor is much lower than at 0°; as shown in Table XLIV it falls as low as 0.4, and never rises above 1.0.

The influence of the concentrations of the various reagents on the factor is in accordance with the supposition[1] that both Fe″ and FeI′ (FeI_2, etc.) are simultaneously undergoing oxidation in the solution; increase in the concentration of the acid, for instance, affects the rate of the second reaction much more than that of the first,[2] and consequently increases the induction factor. A quantitative test of this assumption is postponed until conductivity measurements furnish data for a plausible assumption as to the formula of the addition product (see foot-note, page 634).

My thanks are due to Professor W. Lash Miller, at whose suggestion these measurements were carried out in the Winter of 1907–8.

TABLE XXXVI (HYDROCHLORIC ACID)

Cr, 20; KI, 20; Ox, 5; Fe, 1.0; V, 700; *t*, 0° C

	Expt. 49 HCl, 10	Expt. 5*a*[3] H_2SO_4, 10	Expt. 50 HCl, 20	Expt. 9*a*[3] H_2SO_4, 20
θ	As	As	As	As
0.25	—	—	2.35	4.05
1.0	1.35	1.90	—	7.15
2.0	2.35	3.10	7.70	8.00
4.0	3.90	4.30	—	—

[1] Loc. cit., p. 374.

[2] Ibid., p. 366.

[3] In Expts. 5*a*, 9*a*, etc., the composition of the solution was the same as in Miss Benson's Expts. 5, 9, etc.

TABLE XXXVII (SALTS)

Ac, 10; Cr, 20; KI, 20; V, 700; *t*, 0° C

Expt.	Salt added	Ox	Fe	θ	As	Blank	No. of blank Ex.
51	0.88 g. K_2SO_4	0	1.0	1.0	4.90	5.00	23*a*
52	0.5 g. NaCl	0	1.0	0.5	3.30	3.90	23*a*
53	do	0	0.5	0.5	2.30	2.60	54
55	1.0 g. NaCl	0	1.0	0.5	2.85	3.90	23*a*
56	do	0	0.5	0.5	2.10	2.60	54
57	1.0 g. KBr	0	1.0	0.5	3.30	3.90	23*a*
58	0.03 g. $KF.2H_2O$	5	1.0	4.0	4.40	4.35	5*a*
59	0.1 do	5	1.0	4.0	4.25	4.35	5*a*
60	0.5 do	0	1.0	1.0	0.80	5.00	23*a*
61	1.0 do	0	1.0	1.0	0.20	5.00	23*a*

TABLE XXXVIII (POTASSIUM FLUORIDE)

Ac, 10; Cr, 20; KI (after θ), 20; Ox, 0; V, 700; *t*, 0° C

	Expt. 62 KF, 0		Expt. 63 KF, 1.0[1]		Expt. 64 KF, 3.0		Expt. 65 KF, 5.0		Expt. 66 KF, 10.0	
θ	As	*x*	As	*x*	As	*x*	As	*x*	As	*x*
0.25	3.20	0.65	2.80	0.71	1.60	0.82	0.75	0.90	0.15	0.98
0.50	2.35	0.75	1.80	0.83	0.80	0.91	0.30	0.96	—	—
1.0	1.60	0.84	1.15	0.90	0.40	0.95	—	—	—	—
2.0	1.05	0.90	0.60	0.94	—	—	—	—	—	—
4.0	0.60	0.94	—	—	—	—	—	—	—	—

TABLE XXXVIII B

Fe	KF, 0 As	KF, 1.0 As	KF, 3.0 As	KF, 5.0 As	KF, 10.0 As
1.0	7.20	7.70	7.80	6.20	5.40
0.8	6.15	6.55	6.35	5.20	....
0.6	5.10	5.20	....	4.20	3.60
0.4	3.60	3.70	3.50	2.90	....
0.2	2.00	2.10	1.80	1.60	1.40
0.1	1.00	1.05	0.90	0.80	0.70
0.0	0.00	0.00	0.00	0.00	0.00

[1] KF, 1.0 indicates 10 cc of a solution containing 0.33 gram of potassium fluoride, $KF.2H_2O$ per litre, and is approximately one F-wt of fluoride for one of ferrous salt in the reacting solution.

TABLE XXXIX (COLLOIDS)

Ac, 10; KI, 20; Fe, 1.0; V, 700; *t*, 0° C

Expt. 67 Agar-agar[1] Cr, 20; Ox, 5; θ, 4.0		Expt. 68 albumen[2] Cr, 20; Ox, 0; θ, 1.0		Expt. 69 Dialyzed iron[3] θ, 1.0				
Agar	As	Albumen	As	Cr	Ox	Dial	Total Fe'''	As
0	4.40	0	5.05	10	0	0	0	2.40
5 cc	4.35	50 cc	2.25	10	0	5 cc	10.8	2.00
25	4.45	100	1.15	10	5	0	5	0.80
50	4.40	150	0.55	20	0	0	0	5.05
100	4.40	—	—	20	0	5 cc	10.8	3.50
—	—	—	—	20	5	0	5	1.90

TABLE XL ("AGED" OX PROD)

KI, 20; Cr, 20; Fe, 1.0; V, 700; *t*, 0° C; θ, 1.0

Expt.	Ox	Fe'''	Ac from hydrol.	Ac added	Total Ac	As
70	0	0	0	15	15	7.30
71	5 II	1.0	5.0	10	15	6.70
72	1 I	1.0	0	15	15	6.65
73	5 III	2.87	2.6	10	12.5	4.60
74	2.87 I	2.87	0	12.6	12.6	4.00
75	10 II	2.0	10	0	10	3.20
76	2 I	2.0	0	10	10	3.05
77	0	0	0	0	0	0.00
78	5 I	5.0	0	0	0	0.00
79	0	0	0	10	10	5.05
5*a*	5 I	5.0	0	10	10	1.90
80	10 III	5.74	2.6	0	2.6	0.15

[1] One-tenth percent solution of agar-agar.
[2] One-fifth percent solution of egg-albumen.
[3] 5 cc of the dialyzed iron solution contained 10.8 units.

TABLE XLI (ACID OX PROD)

Ac, 20; Cr, 20; KI, 20; Ox, 5; Fe, 1.0; V, 700; *t*, 30.5° C; Corr, 0.75

Expt.	θ	Ox	As
81	0.25	0	3.35
"	0.50	0	4.05
"	1.0	0	4.70
"	2.0	0	5.25
82	0.25	5 IV	1.35
83	0.25	5 V	1.30
84	0.25	5 I	1.35
82	0.50	5 IV	2.00
83	0.50	5 V	1.90
84	0.50	5 I	2.10
82	1.0	5 IV	2.85
83	1.0	5 V	2.85
84	1.0	5 I	2.85
82	2.0	5 IV	3.85
82	1.0	5 IV[1]	2.85
83	2.0	5 V	3.85
84	2.0	5 I	3.85

TABLE XLII (CORRECTION FOR END POINT AT 30° C)

Expt. 85: Ac, 20; Cr, 20; Ox, 5; Fe, 1.0; V, 700; Iodine 10 cc = As 1.90; *t*, 30.5° C

θ	As found	Corr.
0.25	1.15	0.75
0.50	1.15	0.75
1.0	1.15	0.75
2.0	1.10	0.80
4.0	1.15	0.75
8.0	1.05	0.85

[1] Boiled.

TABLE XLVII

Ac, 20; Cr, 20; KI, 20; Fe, 1.0; V, 700; *t*, 30.5° C

Corr: Expt 94, 0.75; Expt 95, 0.70; Expt 96, 0.72; Expt 97, 0.75; Ex 98, 0.82

θ	Expt. 94 Ox, 0		Expt. 95 Ox, 2.5		Expt. 96 Ox, 3.5		Expt. 97 Ox, 5.0		Expt. 98 Ox, 10.0	
	As	x	As	x	As	x	As	x	As	x
0.25	3.35	0.79	1.55	0.50	1.47	0.55	1.35	0.39	1.12	0.37
0.50	4.05	0.88	2.70	0.76	2.32	0.74	2.00	0.57	1.77	0.58
1.0	4.60	0.95	3.55	0.91	3.12	0.90	2.85	0.80	2.52	0.83
2.0	5.10	1.00	4.20	1.00	3.75	1.00	3.60	1.00	3.05	1.00
9.0	....	....	4.20	1.00	3.75	1.00	3.60	1.00	3.05	1.00
16.0	5.10	1.00	—	—	—	—	—	—	—	—
Blanks:	θ 16, Corr 0.2		θ 9, As 0.80		θ 9, As 1.05		θ 9, As 1.40		θ 4 9 16 As 0.80, 2.40, 5.00	

TABLE XLVII B

Fe	Ox, 0, As	Ox, 2.5 As	Ox, 3.5 As	Ox, 5.0 As	Ox, 10.0 As
0.20	1.70	1.30	1.15	0.80	0.60
0.40	2.75	2.20	2.10	1.50	1.20
0.60	3.85	3.10	2.75	2.30	1.85
0.80	4.60	3.60	3.25	2.90	2.45
1.00	5.10	4.20	3.75	3.60	3.75

TABLE XLVIII

Ac, 20; Cr, 20; KI, 10; Fe, 1.0; V, 700; *t*, 30.5° C

θ	Expt. 99 Ox, 0; Cor. 0.70		Expt. 100 Ox, 5.0; Cor. 0.75		Expt. 101 Ox, 10.0; Cor. 0.70	
	As	x	As	x	As	x
0.25	2.40	0.62	—	—	—	—
0.50	2.95	0.72	1.05	0.40	—	—
1.0	3.75	0.84	1.50	0.60	1.25	0.50
2.0	4.30	0.91	2.48	0.98	1.75	0.70
4.0	5.05	1.00	—	—	2.05	0.85
8.0	5.05	1.00	2.55	1.00	2.30	1.00
Blanks: θ = 8	Cor. 0.35		As, 0.85		As, 1.35	

TABLE XLVIII B ($\theta = 8$)

Fe	Ox, 0 As	Ox, 5.0 As	Ox, 10.0 As
0.20	1.60	0.50	0.30
0.40	2.75	1.05	0.80
0.60	3.75	1.55	1.30
0.80	4.35	2.05	1.80
1.00	5.05	2.55	2.30

TABLE XLIX

Ac, 20; Cr, 10; KI, 20; Fe, 1.0; V, 700; t, 30.5° C

θ	Expt. 102 Ox, 0; Cor. 0.75		Expt. 103 Ox, 5.0; Cor. 0.65		Expt. 104 Ox, 10.0; Cor. 0.82	
	As	x	As	x	As	x
0.25	2.55	0.76	0.80	0.38	—	—
0.50	3.25	0.88	1.35	0.44	1.22	0.40
1.0	3.70	0.95	2.10	0.67	1.87	0.59
2.0	4.10	1.00	2.75	0.82	2.67	0.82
4.0	—	—	3.50	0.99	3.20	1.00
8.0	4.15	1.00	3.65	1.00	3.20	1.00
Blanks: $\theta = 8$	Cor. 0.35		Cor. 0.20		As, 0.20	

TABLE XLIX B ($\theta = 8$)

Fe	Ox, 0 As	Ox, 5.0 As	Ox, 10.0 As
0.20	1.35	1.00	0.65
0.40	2.25	1.80	1.30
0.60	2.95	2.40	1.95
0.80	3.55	3.05	2.60
1.00	4.15	3.65	3.20

List of Experiments

Expt.	Table	Ac	Cr	KI	Ox	Fe	Temp.	Page	
49	36	10	20	20	5	1	0		Hydrochloric acid
50	36	20	20	20	5	1	0		"
51	37	10	20	20	0	1	0		0.88 g. K_2SO_4 added
52	37	10	20	20	0	1	0		0.5 g. NaCl added
53	37	10	20	20	0	0.5	0		"
54	37	10	20	20	0	1	0		"
55	37	10	20	20	0	0.5	0		1.0 g. "
56	37	10	20	20	0	0.5	0		"
57	37	10	20	20	0	1	0		1.0 g. KBr added
58	37	10	20	20	5	1	0		0.03 g. $KF.2H_2O$ added
59	37	10	20	20	5	1	0		0.1 g. "
60	37	10	20	20	0	1	0		0.5 g. "
61	37	10	20	20	0	1	0		1.0 g. "
62	38	10	20	(20)	0	1	0		
63–66	38	10	20	(20)	0	1	0		KF 1.0, 3.0, 5.0, 10.0
67	39	10	20	20	5	1	0		Agar-agar added
68	39	10	20	20	0	1	0		Albumen added
69	39	10	10	20	5&0	1	0		Dialyzed iron added
69	39	10	20	20	5&0	1	0		"
70–80	40	..	20	20	—	1	0		Various aged ox prods added
81–84	41	20	20	20	5&0	1	30.5		Various acid ox prods added
85	42	20	20	—	5	1	30.5		Correction for end point
—	43	—	20	—	5&0	1&0.5	0		Values of Induction factor
—	44	—	..	—	—	1	30.5		"
86–89	45	10	20	20	—	1	30.5		Ox 0, 2.5, 3.5, 5.0
90–93	46	15	20	20	—	1	30.5		"
94–98	47	20	20	20	—	1	30.5		Ox 0, 2.5, 3.5, 5.0, 10.0
99–101	48	20	20	10	—	1	30.5		Ox 0, 5.0, 10.0
102–4	49	20	10	20	—	1	30.5		"

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No. 80: INDIRECT ANALYSIS BY MEANS OF THE DILATOMETER, BY W. LASH MILLER

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INDIRECT ANALYSIS BY MEANS OF THE DILATOMETER: THE "LOWER HYDRATE" OF SODIUM ACETATE

BY W. LASH MILLER

In order to avoid the difficulties which sometimes attend the removal of mother-liquor from the solid products of a reaction,[1] various "indirect" methods of analysis have been devised for determining the composition of the latter.[2]

The method employed in the present paper is different in principle from those hitherto suggested; while less general in its application than some of them, it is perhaps the most convenient in the large group of cases to which it is applicable.

The behavior of crystallized sodium acetate, $C_2H_3O_2Na.3H_2O$, on heating, was first described by Jeannel[3], who found that it begins to melt at 58° C, becomes completely liquid at 75°, and boils at 123°.

When he let the melted salt cool gradually in the air, it crystallized at 58° in prismatic needles, the temperature keeping constant at that point during the crystallization;[4] but if the solution was protected from "germs" it solidified to a white translucent mass of large shiny leaflets covered with a little liquid.

These leaflets were deliquescent in air in which the prismatic salt dried out, and were easily converted into the latter by bringing into dry air, or by touching with a glass rod,

---

[1] Bancroft: Jour. Phys. Chem., 6, 178 (1902); Lash Miller and Kenrick: Ibid, 7, 259 (1903).

[2] v. Bijlert: Zeit. phys. Chem., 8, 343 (1891); Schreinemakers: Ibid., 11, 81 (1893); Kentner: Ibid., 39, 658 (1902); Bancroft: Jour. Phys. Chem., 6, 178 (1902); 9, 558 (1905); Browne: Ibid., 6, 287 (1902).

[3] Comptes rendus, 62, 834 (1866).

[4] Jeannel suggested the use of melted sodium acetate for testing and standardizing thermometers; a note on the suitability of the salt for this purpose will shortly be published.

or with a crystal of "ordinary" sodium acetate—dehydrated sodium acetate had no effect.[1]

Although the supersaturated solutions of sodium acetate have been studied by a large number of authors, among them Reischauer,[2] Gernez,[3] Böttger,[4] Thomson,[5] and Baumhauer,[6] the composition of the leaflets described by Jeannel has not yet been ascertained with certainty. They are commonly referred to in the literature as "a lower hydrate,"[7] and Gernez,[8] though without quoting his authority, gives them the formula $2C_2H_3O_2Na.3H_2O$; but the only analyses of which I have been able to find any account are due to Zettnow.[9]

This chemist melted the commercial acetate in a flask, boiled the liquid, closed the mouth of the flask with cotton wool, and drained the crystals deposited on cooling, by tilting the flask. When the cotton was removed, the (supersaturated) mother-liquor solidified, breaking the flask; the upper layer of crystals was then removed and analyzed, with the following results (in Expts. 3 and 4 the melting was repeated):

TABLE I

Expt.	Water Percent	Formula
1	35.66	$C_2H_3O_2Na$ 2.52 H_2O
–	35.33	" 2.49 "
2	21.33	" 1.24 "
3	18.14	" 1.03 "
–	21.05	" 1.20 "
4	20.04	" 1.14 "
5	32.6	" 2.20 "
6	33.3	" 2.27 "

[1] Berthelot: Comptes rendus, 77, 975 (1873).
[2] Liebig's Ann., 115, 116 (1860).
[3] Jahresbericht, 1865, 75.
[4] Jahresbericht, 1867, 390.
[5] Jour. Chem. Soc., 35, 196 (1879).
[6] Jour. prakt. Chem., 104, 449 (1868).
[7] Ostwald: Lehrbuch II, (2) page 770 (1902)
[8] Comptes rendus, 84, 1389 (1877).
[9] Pogg. Ann., 142, 306 (1871).

The author regards his experiments as establishing the existence of the hydrates $C_2H_3O_2Na.H_2O$, $2C_2H_3O_2Na.5H_2O$, and $2C_2H_3O_2Na.9H_2O$; in the absence of proof that his crystals were free from mother-liquor, however, much weight cannot be attached to these results. The formate and valerate of sodium crystallize with one mol of water, but Thomson's[1] observations that these salts cause no formation of crystals in supersaturated solutions of sodium acetate speaks against the existence of a hydrate $C_2H_3O_2Na.H_2O$.

On repeating Jeannel's experiments it was at once apparent that the "partial melting" at 58° C consists in the complete disappearance of the crystals of trihydrate, and the formation of a solution and of crystals of a new salt (leaflets); a few more experiments, carried out after the manner of Zettnow's, showed that both solution and leaflets, like the trihydrate from which they were formed, were slightly alkaline to litmus. From this observation (which was subsequently confirmed with the crystals separated by the centrifugal apparatus described by Mr. Green)[2] it follows that the leaflets consist of a neutral acetate of sodium, hydrated or anhydrous; as, if they had been formed of an acid or basic acetate, either the crystals themselves or the mother-liquor must have had an acid reaction.

The "partial melting point" of the trihydrate, then, must be considered as the temperature at which the reaction

$$C_2H_3O_2Na.3H_2O = C_2H_3O_2Na.xH_2O + \text{Solution} \ldots \quad (i)$$

is in equilibrium; in other words, it is a transition point in a two-component system, and the following

Considerations based on the phase rule

lead to a method of determining the composition of the crystals in question without removing them from the mother-liquor.

As the existence of equilibrium in heterogeneous sys-

[1] Loc. cit., page 203.

[2] Jour. Phys. Chem., 12, 655 (1908).

tems is not dependent on the quantities of the various phases present, addition of $C_2H_3O_2Na.xH_2O$ in any quantity would cause no change in the temperature of "melting," in the composition of the solution, or in the amount of trihydrate present. Addition of a third hydrate, however, or of the anhydride (supposing x different from 0) renders a new reaction possible, *viz.*, reaction (*ii*), between trihydrate, x-hydrate, and third hydrate (or anhydride); and, as it is very unlikely that both reactions *i* and *ii* will be in equilibrium at the same temperature,[1] it is fair to assume that reaction *ii* will proceed until either the new hydrate or the trihydrate is completely used up.

If y be taken to represent the number of mols of anhydride mixed with A mols of trihydrate, reaction *ii* may be represented by the following chemical equation:

$$\frac{xy}{3-x}(C_2H_3O_2Na.3H_2O) + y(C_2H_3O_2Na) = \frac{xy}{3-x}(C_2H_3O_2Na.xH_2O) \qquad (ii)$$

which shows that $xy/(3-x)$ mols of the trihydrate would disappear, leaving only $A-xy/(3-x)$ mols to enter into reaction *i*.

A determination of the residual trihydrate, therefore, together with the known values of A and y, is sufficient to determine x, that is, the composition of the crystals formed by melting the trihydrate at 58° C.

The easiest way to determine the amount of trihydrate in a mixture of trihydrate and x-hydrate is to heat to 58° and measure the change of volume which accompanies the "melting." This is obviously proportional to the amount of trihydrate present; by means of a blank experiment, in which the dilatometer is filled with a known quantity of the pure trihydrate, the weight of that salt corresponding to one division of the dilatometer scale may be ascertained.

[1] The statement of the phase rule, that in a two-component system at arbitrary pressure not more than three phases can exist in equilibrium, is only another way of putting this.

Dilatometer measurements

To facilitate the introduction of weighed amounts of salt into the dilatometer, the bulb of the latter was replaced by a cylindrical vessel closed by a perforated cork with capillary through which the (dried and air-free) coal oil was sucked into the instrument; contrary to expectation, there was no trouble due to swelling of the cork when the whole was immersed in the water bath.

Two sets of measurements were carried out: the first with 4.040 grams of the pure trihydrate, and the second with 3.350 grams of a mixture prepared by grinding trihydrate and anhydride together, heating for some time above 60°, cooling, and powdering again. The amount of water in this mixture was determined by heating to 120° until the weight was constant:

Weight before heating	1.7156 g.
Weight after heating	1.4460

TABLE II

4.040 g. trihydrate			3.350 g. mixture		
Interval Hrs. min.	Temp.	Dilatr. div'ns	Interval Hrs. min.	Temp.	Dilatr. div'ns
— 30	56.6° C	47.0	— 7	57.0° C	123.0
— 27	57.0	48.0	— 7	57.5	126.0
— 11	57.5	51.0	— 5	58.0	131.5
— 8	58.0	53.0		58.5	143.0
3 12	58.5	56.8		Heated to 75°	
17 0	59.0	227.0	1 4	59.5	188.0
1 10	59.35	229.0		58.8	187.5
1 5	58.7	228.0			
	56.3	220.0	(Interp)	58.0	187.0 melted
				58.0	131.5 solid
(Interp)	58.0	224.5 melted			
	58.0	53.0 solid		Expansion	55.5
Expansion		171.5			

Assuming that the melting takes place at 58° on the thermometer employed, the first experiment shows that

the expansion per gram of trihydrate melted is 42.44 divisions of the dilatometer scale. The expansion of the mixture, 55.5 divisions, corresponds to 1.308 grams of trihydrate or 0.009616 mols.

Thus $A-xy/(3-x) = 0.009616$. The values of A and y, calculated from the weight and composition of the mixture, are 0.009750 and 0.02346, respectively; from which it follows that $x = 0.017$, or that the composition of the "x-hydrate" is $C_2H_3O_2Na.\ 0.017H_2O$.

The reliability of this result obviously depends on the accuracy of the dilatometer measurements. The error of each of the expansions measured is probably at least one scale division, but certainly less than five divisions; while even if 5 divisions be added to the expansion of the trihydrate and 5 be subtracted from that of the mixture—the most unfavorable combination—the value of x rises only to 0.16.

The measurements therefore prove conclusively that the crystals deposited by the trihydrate on "melting" consist of anhydrous sodium acetate.

The University of Toronto,
June 1908.[1]

[1] Read before the American Chemical Society at the Buffalo Meeting September 1905, under the title "A new use for the Dilatometer."

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PAPERS FROM THE CHEMICAL LABORATORIES

No. 81: THE "MELTING-POINT" OF HYDRATED SODIUM ACETATE, BY W. F. GREEN

(REPRINTED FROM THE JOURNAL OF PHYSICAL CHEMISTRY, VOL. XII)

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THE "MELTING-POINT" OF HYDRATED SODIUM ACETATE: SOLUBILITY CURVES

BY W. F. GREEN

In the preceding paper Professor Lash Miller has shown that the composition of the crystals formed by "melting" sodium acetate trihydrate may be ascertained by means of dilatometer measurements, without isolating the crystals from the solution; the following experiments were undertaken to obtain evidence in confirmation of the result there arrived at—*viz*: that "Jeannel's leaflets" are anhydrous sodium acetate.

Isolation of the leaflets

The first attempts were made by centrifuging the mixture of leaflets and (supersaturated) mother-liquor;[1] the crystals left behind all proved to contain water (Table I,*a*), in one case more than the least found by Zettnow. That this water was due to residual solution—partly, at all events—was shown by dissolving a little rosaniline acetate in the melt; after cooling and centrifuging, the inner layers of crystals were quite colorless; but those next the cork were strongly tinged with red, showing how difficult it is to remove the viscous mother-liquor, and readily explaining the large percentage of water left in Zettnow's preparations, which were dried merely by draining in the cold.

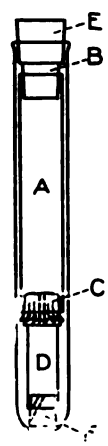

Fig. 1

[1] The apparatus employed is represented in Fig. 1, it was designed to prevent access of dust to the supersaturated solution. The inner tube *A* was filled with the trihydrate and closed at the ends with the corks *b* and *c*, of which *c* was perforated and covered with hardened filter paper. The whole was then inserted in the outer tube, which contained a short piece of thick glass tubing *D*, provided with a perforated rubber stopper, the outer tube was then corked, *E*, and left standing, *E* down, in a steam bath until the acetate was melted. After cooling, the apparatus was placed in the centrifuge, *D* outwards, and the mother-liquor separated from the crystals which remained inside *A*.

A hundred grams of the hydrated acetate was then melted in a cylindrical tap funnel, the mouth of which was closed with a plug of cotton wool. After cooling to 15° the stem was filled with water to prevent the entrance of "germs," and connected with a vacuum pump; in this way most of the liquid was removed. The crystals were then drained for some hours in a steam bath at 95° the tap of the funnel being left open, and finally as much as possible of the remaining mother liquor was pumped off hot. On cooling, the upper part of the funnel was found to be filled with a white crust, and the bottom with moist crystals (Table I,*c*), but the crystals in the middle of the funnel retained their form and were transparent, bright and sharp, showing conclusively that they had suffered no change by being heated to 95°, but were identical with the "leaflets" deposited at 15°. Analysis showed them to be anhydrous (Table I,*b*).

Prepared in this manner, the crystals form either thin plates or long thin needles;[1] their melting-point[2] was identical with that of a sample of anhydrous acetate prepared by dehydrating the trihydrate and melting the salt so obtained; both melted at 322° to 324° uncorr.; Schaffgotsch[3] gives 319° as the melting-point of $C_2H_3O_2Na$.

Solubility determinations

Solubility of the Anhydrous Salt.—For temperatures above 58° the determinations were made in an open test-tube of 100 cc capacity, in which the crystals prepared as just described were stirred with water by a strip of window glass bent into a spiral and fused to a glass rod. The apparatus stood in a thermostat, except for the determination at 123° when the contents of the tube were boiled over a Bunsen flame.

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[1] According to Haushoffer (Zeit. f. Krystallogr., 4, 572 (1880)) sodium acetate crystallizes from alcoholic solution in spear-formed needles and in plates.

[2] Determined in a capillary tube, with high-temperature mercury thermometer, in a bath of anthracene which had recently been distilled to make it transparent.

[3] Pogg. Ann., 102, 293 (1857).

A warmed glass tube, constricted about ¼ inch above its lower end which was filled with a loose plug of absorbent cotton, served to remove a portion of the solution for analysis; the lower end of the tube was quickly cut off with a pair of scissors, and the solution blown out into a weighed crucible, which was immediately covered and weighed again. The water was driven off without spirting by heating for some hours in a steam bath at 95° and then to constant weight at 120°. The results are given in grams of anhydrous salt per 100 g water, and are in most cases the means of accordant determinations.

At temperatures below 58°, where the solutions are supersaturated with respect to the trihydrate, the combination of tap funnel *A*, adapter *B*, and vial *C* shown in Fig. 2 was employed. A quantity of trihydrate was melted in the funnel, the apparatus set together and tied to the piece of board weighted at *G*, and was rocked about the axis *H* in a thermostat over night. A partial vacuum was then created in the adapter by means of a rubber tube attached to *F*, the tap *D* was opened a little and the vial filled. The tap was then closed and the whole removed from the thermostat; the stopper *E* and vial removed, part of the solution quickly poured into a crucible and treated as described. After washing and drying vial and adapter, the apparatus was ready for another determination.

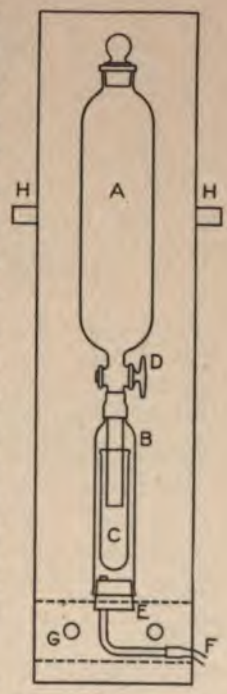

Fig. 2

Solubility of the Trihydrate.—These measurements were made in the open vessel used for the anhydrous salt above 58°; the results are expressed in the same units as before, *viz.*: grams of anhydrous salt to 100 grams of water in the solution. Four numbers are taken from Schiavon[1] and one from Guthrie.[2]

[1] Gazz. Chim. Ital., 32, 532 (1903).
[2] Phil. Mag. [5], 2, 215 (1876).

Table III gives the solubilities for every 10°, obtained by graphic interpolation from the figures of Table II. The data for the freezing-point and boiling-point curves are taken from tables by Legrand[1] and Guthrie,[2] respectively. The four curves in Fig. 3 give the compositions of solutions saturated with anhydride, trihydrate, ice, and steam at atmospheric pressure, respectively.

TABLE I

Expt.	Water Percent	Mols H_2O to one mol $C_2H_3O_2Na$	
	18.14	1.03	Zettnow's driest
a	33.0	2.24	Centrifuged
	5.4	0.3	Centrifuged
b	0.6	0.03	Drained hot
	0.37	0.016	Drained hot
	0.36	0.016	Drained hot
c	4.0	0.22	Bottom of funnel

TABLE II

Anhydrous				Trihydrate		
0°	119	72°.5	149	0°	36.2	Guthrie
25	125	83	154.3	9	40	Schiavon
34.8	129	83.5	154.3	13	43.5	Schiavon
43	131	100	170	37	61.0	Schiavon
50	133.5	123	193	41	68.0	Schiavon
61	140.5	—	—	51.5	87.5	Green
—	—	—	—	55.5	102	Green

TABLE III

Temp.	-18°	-10°	0°	10°	20°	30°	40°	50°	58°
Ice	30.4	19.0	0	—	—	—	—	—	—
Hydrate	30.4	33.0	36.3	40.8	46.5	54.5	65.5	83	138
Anhydrous	—	—	119	121	123.5	126	129.5	134	138
Temp.	60°	70°	80°	90°	100°	110°	120°	123°	
Anhydrous	139.5	146	153	161	170	180	191	193	
Steam	—	—	—	—	0	69	156	193	

[1] Lieb. Ann., **17**, 36 (1836); see also Gerlach: Zeit. anal. Chem., **26**, 455 (1887).

[2] Loc. cit. See also Rüdorff: Pogg. Ann., **145**, 616 (1872).

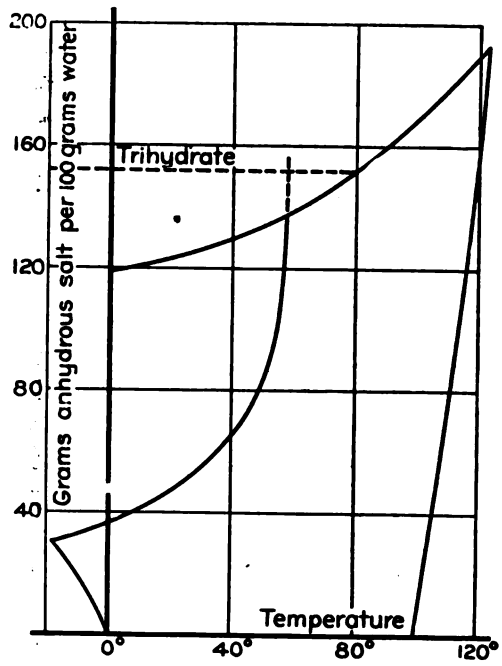

Fig. 3

Summary

The crystals deposited from supersaturated solutions of sodium acetate trihydrate have been isolated and analyzed; in confirmation of the results obtained by dilatometer measurements they consist of anhydrous sodium acetate. The crystalline form and the melting-point of the salt so obtained are those of ordinary anhydrous sodium acetate.

The solubility of the anhydrous salt has been determined from 0° to 123°—the boiling-point of the saturated solution; and that of the trihydrate from the cryohydratic point (Guthrie) to its "melting-point."

The "melting-point" of the trihydrate is a transition point, at which the reaction

$$C_2H_3O_2Na.3H_2O = 0.092\ C_2H_3O_2Na + \text{Sol'n}\ (0.908\ C_2H_3O_2Na + 3H_2O)$$

is in equilibrium. As noted by Jeannel, the "melting" at 58° is incomplete; the lowest temperature at which a clear solution can be obtained is obviously that at which the solution saturated with the anhydride has the same composition as the crystals of the trihydrate, *viz.*: 152 grams salt to 100 grams water. This is the case at 79°, where the dotted line corresponding to the composition of the trihydrate in Fig. 3 cuts the solubility curve of the anhydrous salt; Jeannel gives 75°, Zettnow 77° to 78°.

The "true melting-point," at which trihydrate is in equilibrium with a solution of its own composition, would be given by the intersection of the same dotted line with the solubility curve, produced, of the trihydrate. This temperature would be very little higher than that of the transition point, as at the true melting-point the tangent to the solubility curve must be perpendicular.

These measurements were carried out under the direction of Prof. W. Lash Miller in the chemical laboratory of the University of Toronto in the spring of 1903.

The University of Toronto
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PAPERS FROM THE CHEMICAL LABORATORIES

No. 82: THE HYDRATES AND ACID SALTS OF FERROUS SULPHATE, BY FRANK B. KENRICK

(REPRINTED FROM THE JOURNAL OF PHYSICAL CHEMISTRY, VOL. XII)

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THE HYDRATES AND ACID SALTS OF FERROUS SULPHATE

FRANK B. KENRICK

A large number of ferrous sulphates have been described by various authors. The following are mentioned, with references, by Dammer:[1] $FeSO_4 7H_2O$, $FeSO_4 5H_2O$, $FeSO_4 4H_2O$, $FeSO_4 3H_2O$, $FeSO_4 2H_2O$, $FeSO_4 H_2O$, $FeSO_4$, $FeSO_4 H_2SO_4 6H_2O$, $FeSO_4 5H_2SO_4 5H_2O$ and FeS_2O_7. Many of these were prepared in contact with sulphuric acid of considerable concentration, and as this is extremely difficult to separate from the solid substance and as the analyses were often made after drying either by a current of air (Jeremin, $FeSO_4 H_2O$ and $FeSO_4 5H_2SO_4 5H_2O$)[2] or over concentrated sulphuric acid (Bolas, "Ferrous anhydro-sulphate," FeS_2O_7)[3], it is quite probable that the formulae given by these authors do not in all cases represent the true composition of the solid phases. The following experiments were carried out with the hope of fixing more definitely the composition of some of the ferrous sulphates stable in contact with solutions of sulphuric acid.

Method.—Powdered recrystallized ferrous sulphate ($FeSO_4 7H_2O$) was mixed with sulphuric acid of various concentrations in glass stoppered bottles and shaken at room temperature in a mechanical shaker until the composition of the liquid became constant. Glass marbles were added to each bottle to aid the stirring. To prevent oxidation, which in the longer experiments was found to be quite appreciable, the free spaces in the bottles were filled with nitrogen by blowing in a rapid stream of this gas before inserting the vaselined stoppers. The nitrogen was prepared from ammonium chloride, sodium nitrite and potassium bichro-

[1] Handbuch anorg. Chemie, III, 329, 330, 337 (1893).
[2] Ber. chem. Ges. Berlin, 21, R. 590 (1888).
[3] Jour. Chem. Soc., 27, 212 (1874).

mate, washed by ferrous sulphate and soda lye, and kept in a gas-holder over weak lye.

After equilibrium was established and the bottles had stood upright for a day or so, the solid, which slowly settled to the bottom as a paste, was sucked up into a centrifuge tube. This was a cylindrical glass tube, temporarily closed at both ends by rubber stoppers carrying tubes of small bore. Immediately the tube was full, the temporary stoppers were replaced by rubber plugs faced with platinum discs. After centrifuging for 20 minutes, the plug at the upper end was removed, the liquid poured quickly into a weighing bottle and the plug immediately replaced. The other plug was next taken out, and the first plug pushed through the cylinder thus forcing out the cake of paste which was caught in the weighing bottle. In this way the contents of the centrifuge were transferred to the weighing bottles without more than a couple of seconds' exposure to the moisture of the atmosphere.

Determination of Composition of the Solid Phase.—Two methods were adopted for ascertaining the composition of the solid phases. Each alone is insufficiently accurate to settle definitely the composition, but together they afford a solution of the problem.

The first method consisted in analyzing liquid and wet solid over a range of varying composition of the liquid phase and obtaining the composition of the dry solid graphically from pairs of such analyses. Unfortunately, the difficulty of separating the liquid from the solid and the small range of concentration of liquid possible in some of the cases investigated combine to magnify enormously the effect of experimental error on the composition of the solid. For example, in the case of the compound $2FeO_3SO_3 2H_2O$,[1] taking the most favorable possible pair of analyses, an error of 0.1 percent in the determination of the SO_3 in one of the

[1] With this substance, the paste always contained from 65–75 percent of liquid phase after centrifuging. Even after leaving it on a porous plate in an exsiccator over the mother-liquor as much as 60 percent remained.

pastes, would cause an error of about 6 percent in the ratio of H_2O to SO_3 in the dry solid. By the ordinary gravimetric method of determining SO_3 in the presence of iron it was not found possible to obtain results sufficiently accurate for the purpose, but a method based on specific gravity determinations, described below, proved quite satisfactory. (Duplicates agreed consistently to 0.1 percent.)

The second method adopted, consisted in adding to the mixture a "tell-tale" substance which dissolved in the liquid without entering into the composition of the solid phase, and determining the quantity of the liquid in the wet solid from the amount of the tell-tale found. For this purpose, ammonium sulphate was used. It was hoped that by using different tell-tales in duplicate experiments their non-participation in the solid could be proved from the identity of the composition calculated for the solid phase, but a satisfactory second tell-tale substance was not found. However, by adding the ammonium sulphate in small quantities after equilibrium was established the chance of its forming solid solutions was minimized. The far greater analytical errors of this method are partly compensated for by their much smaller effect on the result. For example, taking, as before, the case of $2FeO3SO_32H_2O$, an error of 0.1 percent in the SO_3 in the wet solid would cause an error of only about 1.5 percent in the ratio of H_2O to SO_3 in the dry solid. On the ratio of FeO to SO_3, both of which were determined directly, the effect of the error is much smaller, and the method serves to give this ratio with a fair degree of accuracy.

Composition by Specific Gravity Method.—Stock solutions of sulphuric acid and of ferrous sulphate were prepared and carefully analyzed—the former gravimetrically and the latter by permanganate. With these, a number of solutions were made up, all containing 0.000499 formula weights FeO per gram but varying quantities of SO_3. The specific gravity of these was found at 25.0° in a 20 cc pyknometer. The results are expressed by the interpolation formula:

$$y = 41.07 + 1.2643\,x - 0.001865\,x^2 + 0.000004257\,x^3,$$

where y = grams of SO_3 per kilo of solution and x = (sp. gr. / 1000) — 1080. The specific gravity is compared with water at 25° and uncorrected. In making the analyses of the wet solids, a weighed quantity of water, sufficient to effect solution, was added to the substance and the FeO determined in a portion of this liquid by n/10 permanganate. Enough water was then added to reduce the concentration of the iron to that to which the interpolation formula applied, and finally the specific gravity of the solution taken. The SO_3 in the wet solid was calculated from the formula, the FeO from the permanganate reading, and the water by difference.

The liquid phases, except those in equilibrium with tetra- and heptahydrates, contained only traces of iron. In these it was found that the SO_3 could be determined quite accurately with n/5 potassium hydroxide. The small quantity of iron was precipitated and oxidized to ferric hydroxide; directly, excess of alkali was added and had no effect on the end-point. The results of the analyses are given in the following table.

TABLE I[1]

Number	Receipt	Comp. of liquid. To 1 SO_3	Comp. of wet solid. To total of 1 formula weight	Solid phase
1	Residue[2] 370 cc acid[3] 120 cc fuming acid	1.122 H_2O 0.0002 FeO	0.0494 FeO 0.4835 SO_3 0.4671 H_2O	$FeO_4SO_3 3H_2O$
2	Residue 450 cc acid	1.226 H_2O 0.0004 FeO	0.0428 FeO 0.4695 SO_3 0.4877 H_2O	$FeO_4SO_3 3H_2O$

[1] In Experiments 1–4 another interpolation formula was used corresponding to a smaller concentration of FeO. In Exps. 20–22 the SO_3 was determined directly as barium sulphate.

[2] By "residue" is meant the wet solid made by shaking 40 grams ferrous sulphate heptahydrate with 470 cc concentrated sulphuric acid and pouring off the liquid.

[3] By "acid" is meant chemically pure sulphuric acid, specific gravity 1.84.

TABLE I—(*Continued*)

Number	Receipt	Comp. of liquid. To 1 SO_3	Comp. of wet solid. To total of 1 formula weight	Solid phase
3	20 gram salt[1] 460 cc acid	1.275 H_2O 0.0005 FeO	0.0497 FeO 0.4632 SO_3 0.4871 H_2O	$FeO4SO_33H_2O$
4	Identical with No. 2 + 15 cc water	1.342 H_2O ? FeO	0.0434 FeO 0.4391 SO_3 0.5175 H_2O	$FeO2SO_3H_2O$
5	40 gram salt 400 cc acid	1.382 H_2O ? FeO	0.0737 FeO 0.4676 SO_3 0.4587 H_2O	$FeO4SO_33H_2O$ probably in unstable equilib.
6	20 gram salt 200 cc acid	1.407 H_2O 0.0008 FeO	0.1120 FeO 0.4550 SO_3 0.4330 H_2O	$FeO2SO_3H_2O$
7	30 gram salt 200 cc acid	1.456 H_2O 0.0009 FeO	0.1153 FeO 0.4482 SO_3 0.4365 H_2O	$FeO2SO_3H_2O$
8	45 gram salt 200 cc acid	1.595 H_2O 0.0013 FeO	0.1191 FeO 0.4372 SO_3 0.4437 H_2O	$FeO2SO_3H_2O$
9	55 gram salt 200 cc acid	1.637 H_2O 0.0014 FeO	0.0690 FeO 0.3902 SO_3 0.5408 H_2O	$2FeO3SO_32H_2O$
10	60 grams salt 200 cc acid	1.697 H_2O 0.0014 FeO	0.0634 FeO 0.3866 SO_3 0.5500 H_2O	$2FeO3SO_32H_2O$
11	85 grams salt 200 cc acid	1.822 H_2O 0.0011 FeO	0.0632 FeO 0.3678 SO_3 0.5690 H_2O	$2FeO3SO_32H_2O$
12	100 grams salt 200 cc acid	1.951 H_2O 0.0010 FeO	0.0636 FeO 0.3591 SO_3 0.5773 H_2O	$2FeO3SO_32H_2O$
14	90 grams salt 150 cc acid	2.209 H_2O 0.0011 FeO	0.0853 FeO 0.3442 SO_3 0.5705 H_2O	$2FeO3SO_32H_2O$

[1] By "salt" is meant recrystallized ferrous sulphate heptahydrate.

TABLE I—(*Continued*)

Number	Receipt	Comp. of liquid. To 1 SO_3	Comp. of wet solid. To total of 1 formula weight	Solid phase
13	112.5 grams salt 150 cc acid	2.186 H_2O 0.0011 FeO	0.1770 FeO 0.3462 SO_3 0.4768 H_2O	Two phases: $2FeO3SO_32H_2O$ $FeOSO_3H_2O$
15	75 grams salt 150 cc acid 26 cc water	2.385 H_2O 0.0006 FeO	0.1496 FeO 0.3134 SO_3 0.5370 H_2O	$FeOSO_3H_2O$
16	75 grams salt 150 cc acid 41 cc water	2.685 H_2O 0.0004 FeO	0.1718 FeO 0.3016 SO_3 0.5266 H_2O	$FeOSO_3H_2O$
17	60 grams salt 120 cc acid 56 cc water	3.200 H_2O 0.0005 FeO	0.1366 FeO 0.2750 SO_3 0.5884 H_2O	$FeOSO_3H_2O$
18	60 grams salt 120 cc acid 80 cc water	3.921 H_2O 0.0006 FeO	0.1285 FeO 0.2531 SO_3 0.6184 H_2O	$FeOSO_3H_2O$
19	80 grams salt 100 cc acid 100 cc water	5.107 H_2O 0.0021 FeO	0.1119 FeO 0.2210 SO_3 0.6671 H_2O	$FeOSO_3H_2O$
20	28 grams salt 7 cc acid 15 cc water	7.93 H_2O 0.106 FeO	0.197 FeO 0.236 SO_3 0.567 H_2O blue crystals dried 1 FeO 1.001 SO_3 6.974 H_2O	Two phases: $FeOSO_3H_2O$ $FeOSO_37H_2O$
21	28 grams salt 7 cc acid 15 cc water	8.97 H_2O 0.142 FeO	Dried crystals 1 FeO 1.004 SO_3 4.15 H_2O	$FeOSO_34H_2O$
22	28 grams salt 3 cc acid 20 cc water	15.0 H_2O 0.287 FeO	Dried crystals 1 FeO 0.999 SO_3 7.11 H_2O	$FeOSO_37H_2O$

Explanation of Table I.—The numbers in the first column correspond with the numbers in the triangular diagram (See Figure) in which each corner represents one formula weight of the substance marked.

The second column contains the receipts by which the mixtures were made up (See foot-notes).

In the third column, the composition of the liquid phase is given in formula weights of H_2O and FeO to one SO_3.

Column four shows the composition of wet solid in formula weights of each constituent to a total of one formula weight (except in the case of the dried crystals, Exps. 20–22).

The last column shows the most probable formula of the solid phase.

Discussion of Results.—The lines for Exps. 1, 2, 3 and 5 meet very nearly in the point corresponding to the compound $FeO4SO_33H_2O$ (See Figure), and this formula is definitely confirmed by Exp. 23 of the next section (See Table II).

In Exps. 4, 6, 7 and 8, the lines converge in the direction of the point corresponding to $FeO2SO_3H_2O$, but the angle made by the lines is so small that the compounds $4FeO6SO_3H_2O$ or even the anhydrous $3FeO4SO_3$ (marked with crosses on the diagram) might also be said to represent the point of convergence. Exps. 24, 25 and 26 of the next section, fix the ratio of FeO to SO_3 as $FeO2SO_3$; hence the formula $FeO2SO_3H_2O$ represents the composition of the solid. The result of Exp. 4 is doubtful. The solid phase in the bottle was undoubtedly identical with that in Exps. 1, 2 and 3, both in texture of the paste and in microscopic appearance. The position of the points can only be accounted for by the assumption that the solid was in unstable equilibrium and changed in the centrifuge to the $FeO2SO_3H_2O$.

In Exps. 9, 10, 11, 12 and 14 the meeting point of the lines is not well-marked, probably owing to the large portion of liquid in the pastes analyzed, but the irregularity of the directions does not warrant the assumption of a solid solution. The points corresponding to the formulae $FeOSO_3$, $3FeO\ 4SO_32H_2O$, $2FeO3SO_32H_2O$, $3FeO5SO_34H_2O$, $FeO2SO_32H_2O$,

etc., in which the ratio of FeO to SO_3 increases from 1 : 1 to 1 : 2, all lie in the general direction of the lines. Exps. 27 to 30, below, point to the ratio $2FeO : 3SO_3$ (possibly $3FeO : 5SO_3$) as the most probable, corresponding with the formula $2FeO3SO_32H_2O$ (possibly $3FeO5SO_34H_2O$).

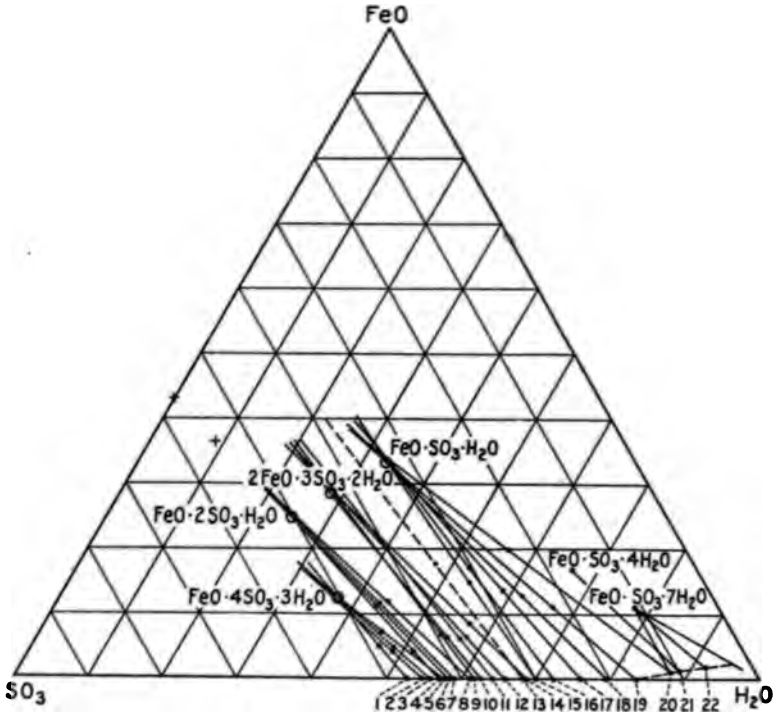

Fig. 1

In Exp. 13, two solid phases were distinctly seen under the microscope.

Exps. 15 to 20 leave little doubt that the corresponding solid phase in these cases is $FeOSO_3H_2O$. This formula is confirmed by Exp. 31, below.

In Exp. 20, the solid consisted of two phases, one, blue and the other white. The blue crystals were picked out, dried with filter paper, and found to be heptahydrate (in unstable equilibrium). The white paste was analyzed and gave the point in the diagram on the line drawn towards

$FeOSO_3H_2O$. On another occasion, the same mixture gave the result shown in Exp. 21, namely, the tetrahydrate. A detailed investigation of the salts in equilibrium with these weaker acids was not made.

Composition by Ammonium Sulphate Method.—In these experiments, FeO, SO_3, $(NH_4)_2O$ and H_2O were determined in both liquid and wet solid. The iron was determined by permanganate, the sulphuric acid as barium sulphate after removing the iron by precipitating twice with ammonia, and the small amount of ammonium by distilling with excess of lye and titrating the distillate. The water was determined by difference. The ratio of ammonium in liquid and wet solid, which unfortunately could not be determined very accurately, gave the amount of liquid in the wet solid. The results calculated for the dry solids are given in the following table. The values for the water, on which the effect of experimental error is greatest, are too inaccurate to be of much use, but the ratio of FeO to SO_3 is sufficiently accurate to enable one to decide between the various possible formulae given by the *direction* of the lines in the former method.

Explanation of Table.—The second column gives the receipts by which the mixtures were made up. For the meaning of the words Residue, Acid and Salt see foot-note to Table I. Under the heading "Ammonium Ratio" is given the ratio of $(NH_4)_2O$ in the wet solid to that in the solution, *per gram.*

The results have been discussed above in connection with the experiments in Table I.

Description of the solid phases.—The substance $FeOSO_3H_2O$ consists of very minute uniformly sized granular crystals about 0.001 mm in diameter. It is stable in contact with solutions of compositions from $SO_3 2.186H_2O$ to $SO_3 7.93H_2O$, at which point (in Exp. 20) the heptahydrate was formed. It is identical with the compound described by Jeremin[1] and may correspond with v. Bonsdorf's $FeSO_4H_2SO_4 6H_2O$, (A mixture of $FeOSO_3H_2O$ with 52.5 percent of solution $SO_3 6H_2O$ has this composition.)

[1] Ber. chem. Ges. Berlin, **21**, R, 590 (1888).

TABLE II

Number	Receipt	Comp. of liquid. Formula weights to 1 SO_3	Comp. of wet solid. Formula weights per gram	Ammonium ratio	Comp. of dry solid
23	Residue 400 cc acid 20 g Am. sulph.	1.23 H_2O 0.0004 FeO 0.0222 $(NH_4)_2O$	0.001051 FeO 0.00940 SO_3 0.00921 H_2O 0.000115 $(NH_4)_2O$	0.537	1 FeO 4.000 SO_3 2.7 H_2O
24	20 g Salt 200 cc Acid 20 g Am. sulph.	1.28 H_2O 0.0005 FeO 0.0414 $(NH_4)_2O$	0.001532 FeO 0.00892 SO_3 0.00903 H_2O 0.000244 $(NH_4)_2O$	0.621	1 FeO 1.99 SO_3 0.964 H_2O
25	20 g Salt 200 cc Acid 10 g Am. sulph.	1.304 H_2O 0.0005 FeO 0.0210 $(NH_4)_2O$	0.001665 FeO 0.00897 SO_3 0.00865 H_2O 0.000119 $(NH_4)_2O$	0.592	1 FeO 1.997 SO_3 0.77 H_2O
26	20 g Salt 200 cc Acid 10 g Am. sulph.	1.345 H_2O 0.0005 FeO 0.0213 $(NH_4)_2O$	0.002433 FeO 0.00849 SO_3 0.00783 H_2O 0.0000788 $(NH_4)_2O$	0.390	1 FeO 1.97 SO_3 1.18 H_2O
27	30 g Salt 50 cc Acid 3 g Am. sulph.	1.98 H_2O 0.001 FeO 0.0245 $(NH_4)_2O$	0.001036 FeO 0.00824 SO_3 0.0142 H_2O 0.000169 $(NH_4)_2O$	0.787	2 FeO 3.25 SO_3 0.6 H_2O

TABLE II—(*Continued*)

Number	Receipt	Comp. of liquid. Formula weights to 1 SO_3	Comp. of wet solid. Formula weights per gram	Ammonium ratio	Comp. of dry solid
28	35 g Salt 120 cc Acid 4 g Am. sulph.	1.66 H_2O 0.001 FeO 0.0145 $(NH_4)_2O$	0.001655 FeO 0.00826 SO_3 0.0116 H_2O 0.000083 $(NH_4)_2O$	0.633	2 FeO 3.04 SO_3 2.54 H_2O
29	55 g Salt 200 cc Acid 10 g Am. sulph.	1.62 H_2O 0.001 FeO 0.0220 $(NH_4)_2O$	0.00213 FeO 0.00820 SO_3 0.0102 H_2O 0.000098 $(NH_4)_2O$	0.695	2 FeO 2.94 SO_3 2.7 H_2O
30	30 g Salt 90 cc Acid 3 g Am. sulph.	1.69 H_2O 0.001 FeO 0.0144 $(NH_4)_2O$	0.001196 FeO 0.00846 SO_3 0.0128 H_2O 0.0000959 $(NH_4)_2O$	0.742	2 FeO 3.04 SO_3 2.63 H_2O
31	40 g Salt 50 cc Acid 50 cc Water 10 g Am. sulph.	4.74 H_2O 0.002 FeO 0.01121 $(NH_4)_2O$	0.00322 FeO 0.00589 SO_3 0.0156 H_2O 0.000298 $(NH_4)_2O$	0.466	1 FeO 0.987 SO_3 0.84 H_2O

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The substance whose composition is probably $2FeO_3SO_3$ $2H_2O$ consists apparently of fragments of small, extremely thin hexagons from 0.005 to 0.01 mm in diameter. Wet with the liquid phase, they form a very sticky paste. This paste was pure white in most cases, but in some of the earlier experiments where precautions were not taken to exclude the air, it had a distinct greenish tinge, possibly due to traces of ferric iron. It exists in contact with solutions $SO_3 1.637H_2O$ (about) to $SO_3 2.186H_2O$. It is probably the substance described by Jeremin[1] as "greenish shining crystals..very unstable," to which he assigns the formula $FeSO_4 5H_2SO_4 5H_2O$. This may well be so, since a mixture containing the compound with 71.3 percent of liquid phase (of composition $SO_3 2H_2O$) has the composition of Jeremin's substance, and it is "unstable" in the sense that a very slight absorption of water from the atmosphere would cause it to change to the granular $FeOSO_3H_2O$.

The compound $FeO2SO_3H_2O$ exists with solutions $SO_3 1.342H_2O$ to (about) $SO_3 1.595H_2O$. It consists of irregular groups of fine crystals of about 0.005 mm diameter, and is probably the "ferrous anhydrosulphate" of Bolas (FeS_2O_7) which he "dried" over concentrated sulphuric acid.

The compound $FeO4SO_3 3H_2O$ is stable with solutions ranging from the strongest one investigated, $SO_3 1.122H_2O$, to (about) $SO_3 1.342H_2O$. The crystals are fine needles, some of the largest being about 0.2 mm long. They dissolve rapidly in water, precipitating the $FeOSO_3H_2O$.

The solubility of all the compounds in the liquid phases (*i. e.*, the amount of FeO found in the liquids) is, except in the cases of the tetra and heptahydrates, very small. There is a maximum amount of iron at the point corresponding to Exp. 9, and a minimum point near Exp. 17.

Summary.—The compositions of a number of ferrous sulphates and their range of existence with sulphuric acid solutions at ordinary temperatures have been determined.

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[1] Loc. cit.

The composition of the solid phase was obtained by a combination of two methods of indirect analysis, each of which alone was insufficiently accurate for the purpose. In the first method, the analyses of liquids and corresponding wet solids gave the values of a and b in a number of equations to straight lines

$$y = ax + b,\ y = a'x + b',\ \text{etc.},$$

in which y = amount of FeO and x = amount of H_2O to $1SO_3$, and the points on which correspond to possible compositions of the solid phase. In some cases the values of x and y representing the composition of the actual solid, could be determined from the cutting point of these lines; in others the smallness of the angles made this impracticable. In the second method, each analysis of liquid and corresponding wet solid gave the value of y fairly accurately, although the value found for x was too inaccurate to be of any use. By combining the two methods and substituting the value of y given by the second method in any of the equations obtained by the first the value of x could be determined.

University of Toronto,
September, 1908.

UNIVERSITY OF TORONTO STUDIES

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No. 83: THE BEHAVIOUR OF COLLOIDAL SUSPENSIONS WITH IMMISCIBLE SOLVENTS, BY W. LASH MILLER AND R. H. MCPHERSON

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THE BEHAVIOR OF COLLOIDAL SUSPENSIONS WITH IMMISCIBLE SOLVENTS

BY W. LASH MILLER AND R. H. MCPHERSON[1]

Now that the study of colloids is attracting general interest, and convenient methods have been devised for the preparation of colloidal solutions in solvents other than water, it seems desirable to study the behavior of such solutions when brought together, with a view to discovering, if they exist, cases of equilibrium analogous to the distribution of iodine between ether and water.[2]

The prevalent theory of colloidal solutions, which represents them as finely divided suspensions in an inert liquid, seems at first sight to negative the possibility of any such distribution. Graham's experiments,[3] however, and the more recent work of Linder and Picton[4] show that many colloids possess the power of diffusion, *i. e.*, that their chemical potential increases with increase of their concentration;[5] and as, from the point of view of the phase rule, a suspension whose potential depends on its concentration cannot be distinguished from the constituent of a "true" solution, the phenomena of distribution may as legitimately be expected in one case as in the other. Where the change of potential with the concentration is slight, *i. e.*, where the osmotic pressure is small (or the "molecular weight" of the solute or suspension is high), as in the case of the colloids, very slight differences in the properties—surface tension, dielectric constant (Perrin)—of the solvent might be sufficient to offset considerable changes

[1] Read before the section for Physical Chemistry of the American Chemical Society, June, 1908.

[2] Mr. Manning finds that tannin is distributed between water and ether, ethyl acetate, amyl alcohol, etc.; the solutions have measurable osmotic pressure, however, and for other reasons tannin cannot be considered to be a typical colloid.

[3] Phil. Trans., **1861**, 183; fully abstracted in Jahresber. **1861**, 62–82.

[4] Jour. Chem. Soc., **61**, 137 (1892).

[5] The theory advocated by Perrin, which endows the colloid particles with electrical charges, leads to the same conclusion.

in concentration; so that one would expect the distribution to be very one sided, and measurable only under special conditions. These considerations suggest that instances of the distribution of colloids between two solvents are most apt to be discovered by working with colloids of marked diffusibility, and with "immiscible solvents" of almost identical composition—such as the 'critical solutions' in two component systems (phenol, water) or the two phases at the plait point of the binodal curve in three component systems (water, chloroform, alcohol, etc.).

The experiments of Winkelblech on colloids and immiscible solvents made the probability of realizing the ideas set out in the preceding paragraph seem somewhat remote. In a paper published in 1906[1] that author describes "a hitherto unknown reaction for dissolved colloids" which consists in shaking the colloidal solution with petroleum, benzene, chloroform, carbon disulphide, or other immiscible solvent, whereupon the colloidal coagulates and collects in the emulsion which is formed at the surface of separation of the two solvents. This reaction leads to a delicate method for the quantitative determination of gelatine, and succeeds also with glutin, albumen, tannic acid, soluble starch, soap, wine, beer, water-glass, alkaline solutions of colophonium and of sulphur, and solutions of silicic acid in ammonia.

This reaction, if general, would make the experimental study of equilibrium in heterogeneous systems involving colloidal solutions difficult if not impossible. Winkelblech himself, however, has discussed an exception: shaking gelatine solutions with ether does not produce coagulation—and it seemed possible that among the colloidal suspensions (none of which were studied by Winkelblech) others might be found.

Silver, water, isobutyl or amyl alcohol

Our first experiments were tried with colloidal metals prepared by the methods of Bredig[2] and of Svedberg.[3] Silver

[1] Zeit. angew. Chem., **19**, 1953 (1908).
[2] Zeit. phys. Chem., **32**, 127 (1902).
[3] Ber. chem. Ges., **38**, 3616 (1905).

hydrosol is completely coagulated by shaking with commercial amyl alcohol or with isobutyl alcohol (traces of either of which much reduce the surface-tension of water); ***shaking*** however is necessary, merely pouring a layer of the alcohol over the hydrosol does not cause coagulation.

The 'isobutylalcosol' and 'amylalcosol' of silver by shaking with water, likewise are completely coagulated.

Silver, water, phenol

When phenol liquefied by a few drops of water is added to the hydrosol and a homogeneous solution formed by warming, no coagulation takes place even on standing; but if the solution is allowed to cool until it becomes milky from separation into two layers, and is then warmed again until homogeneous, all the silver is precipitated.

These experiments, while not resulting as had been hoped, show the dependence of the Winkelblech effect on the formation of surface, *i. e.*, on capillary forces, and serve to connect it with the separation of fibrin from blood by 'whipping' and with the formation of scum on the surface of streams near waterfalls and rapids.

Silver, water, chloroform, alcohol

When silver hydrosol is shaken with chloroform, very little coagulation takes place and none of the silver goes into the chloroform. Reciprocally, water does not attract silver from the 'chloroformsol.'

On adding alcohol to the systems: hydrosol-chloroform or chloroformsol-water, and shaking to secure equilibrium, most of the silver is coagulated, and what remains in suspension is retained by the layer of liquid in which it was originally present. The chloroform may be replaced by carbon tetrachloride and the silver by gold, without materially modifying the result. These observations seem important, but as it was not found possible to prepare metallic suspensions in chloroform or carbon tetrachloride free from tarry matter, too much stress must not be laid on them.

Arsenic trisulphide, water, chloroform, alcohol

This system is distinguished from the last by the much greater stability of the colloid; the hydrosol may be shaken with chloroform in presence or absence of alcohol, and homogeneous solutions may be "split" or rendered heterogeneous by addition of water or of chloroform without coagulation ensuing. It consequently seemed more suitable for the object in view, and the work with colloidal metals was discontinued.

In the preliminary experiments, whenever two liquid layers were formed the arsenious sulphide was always contained exclusively in the upper layer, no matter what the proportions of the reagents (aqueous solution of arsenious acid, hydrogen sulphide water, alcohol, chloroform). If distribution was to be observed at all, it was therefore necessary to fi d the proportions in which water chloroform and alcohol must be mixed to give two liquid layers of almost identical composition.

Determination of the binodal curve, tie-lines and plait-point

The system water-chloroform-alcohol has been studied by Bancroft[1] to whom in fact is due most of our experimental knowledge of similar equilibria; the data for the curve plotted in Fig. 1, however, were not taken from his measurements which were carried out in a thermostat at 20°, but were obtained directly by a series of determinations made without special precautions at room temperature. The abscissae give the volumes of chloroform (and hence of water, the sum in every case being 10 cc) and the ordinates the volumes of alcohol needed to produce homogeneity. The curve so obtained is the "binodal curve" of Schreinemakers.

When the volume of chloroform used was 3 cc or less, addition of alcohol caused the lower layer to gradually grow less and finally to disappear; when 4 cc or more was used, the upper layer disappeared. The abscissa of the "plait-

[1] Phys. Review, 3, 120 (1895).

point" therefore must lie between 3 and 4. To find its position more accurately, 3.5 cc chloroform and 6.5 cc water were mixed in a tall cylinder of 25 cc capacity graduated in 1/10 cc, alcohol was added from a burette, and, after shaking, the volumes of the two phases were read (see Table 2). Then, through the point in Fig. 1 which represents the total com-

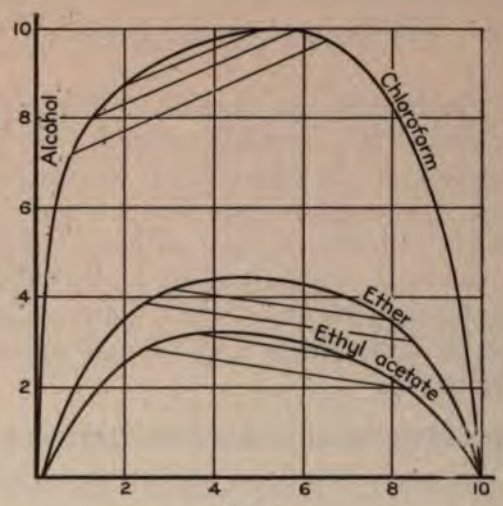

Fig. 1

position of the system, a straight line was drawn terminated at either end by the binodal curve, its direction being so chosen that the lengths of the two portions (to right and left of the abscissa 3.5) stood in the proportion of the volumes of the upper and lower liquid layer respectively.

If in place of the volumes of the two layers their weights had been determined—or what is the same thing, if their specific gravities were the same—the line so drawn would be a "tie-line" and its extremities would give the compositions of the two phases in equilibrium. Near the plait-point the compositions and consequently the densities of the two liquids are almost identical; lower down in the figure the graph gives only a first approximation to the compositions,

which might be improved by introducing the densities calculated from the approximately known compositions of the two layers and the densities of alcohol water and chloroform, neglecting contraction on mixing.

The position of the "plait-point," *i. e.*, the composition of the system in which the two layers of liquid are almost identical in composition, was found graphically, and checked by direct experiment: it is chloroform 3.5 cc, water 6.5 cc, alcohol 9.8 cc.

Arsenic trisulphide, water, chloroform, alcohol, near the plait-point

Solutions were then made up containing 5.5 cc chloroform, 4.5 cc "water" (*i. e.*, 4.5 cc altogether of the solutions of arsenious acid and hydrogen sulphide in various proportions) and alcohol in quantity almost sufficient to make a homogeneous solution. The actual amount of alcohol needed depends on the temperature and also no doubt on the excess of arsenious acid or of hydrogen sulphide present, but it was not far from 9.6 cc. In no case was distribution observed; the sulphide always remained altogether in the upper layer, although in one experiment the compositions of the two phases were so nearly identical that partial separation was effected only by five minutes whirling in a good centrifuge (10 inch arm, 2000 rev. per minute) while complete separation needed a quarter of an hour. In this experiment the total volume was 15 cc, and the volumes of the two phases after separation were almost exactly equal; addition of less than 1/60 0.02 cc of alcohol made the whole homogeneous.

To ascertain whether the arsenious sulphide remained in the upper layer because of some "passive resistance," pairs of solutions—upper and lower—were made up from the data of Fig. 1, using pure water in the preparation of the "upper" and the solutions of arsenious acid and hydrogen sulphide in the preparation of the "lower" layers. On mixing, while the volumes of the two layers remained unaltered, the arsenious sulphide passed completely from the

lower to the upper layers. "Passive resistances" therefore cannot be invoked to explain the very one sided distribution observed.

The slight difference in composition and properties of the two liquids evidently determined the distribution of the arsenious sulphide at equilibrium, from which it follows that the influence of the concentration of the latter on its chemical potential must be slight indeed—a calculation based on Perrin's theory and on measurements of the dielectric constants of the boundary solutions near the plait-point might lead to a lower limit for the 'molecular weight' of the sulphide.

Arsenic trisulphide, water, chloroform, acetone

The alcohol of the preceding sections was replaced by acetone; but, as before, the arsenious sulphide remained in the upper layer until the last drop of acetone removed the heterogeneity. The composition at the plait-point is: water 2.9 cc, chloroform 1.0 cc, acetone 8.1 cc.

Arsenic trisulphide, water, ether, alcohol

Tables 1 and 2 and Fig. 1 give the data for the binodal curve, tie-lines and plait-point. A glance at Fig. 1 shows that the ether curve is much flatter, *i. e.*, that in the system ether-water-alcohol, addition of a drop of alcohol produces more change in the compositions of the two layers than it does in the system chloroform-water-alcohol. To approach the plait-point by rough and ready methods is therefore much easier when chloroform is used than with ether; and from this point of view the latter system seem even less likely to afford instances of distribution than the former.

As a matter of fact, however, distribution was readily observed over a fairly wide range of composition on either side of the abscissa of the plait-point. The experiments were carried out by mixing measured volumes of 1 percent arsenious acid solution, ether, alcohol, and sulphuretted hydrogen water (either old or freshly prepared) in the order given, taking somewhat less alcohol than was necessary to make a

homogeneous solution, and then adding more alcohol drop by drop, shaking, and letting stand until the two layers separated. As each drop of alcohol was added and the two layers approached one another in composition, the amount of arsenious sulphide in the upper layer increased until the colors of the two layers were almost equal. More of the sulphide went into the upper layers, other things being equal, when excess of hydrogen sulphide was used; but even with a considerable excess of arsenic (recognized by coagulating the sulphide with a drop of hydrochloric acid, filtering, and treating separate portions of the filtrate with arsenious acid and with hydrogen sulphide respectively) the distribution was easily observable.

Left to themselves, such two layered systems with distributed sulphide may remain for days apparently unchanged; but it was generally observed that sooner or later the upper layer lost its yellow color.

The upper layer is a very clear yellow with a touch of orange, and none of that milkiness usually observed with colloidal solutions; in this respect it resembles Linder and Picton's *Arsenious sulphide δ* which gave no Tyndall effect; the lower layer was almost equally clear. It is, in fact, only with such clear solutions that distribution was observed; if ether and alcohol were added to the ordinary boiled arsenious sulphide hydrosol, which relatively speaking is quite turbid, the sulphide remained in the lower layer until the last drop of alcohol made the whole homogeneous. By adding ether to a two-layered system, the volume of the lower layer may be diminished and the arsenious sulphide in it concentrated. When the concentration reaches a certain point, depending on the composition of the system, a trace of cloudiness may be detected, which increases with further addition of ether; the color at the same time changes from orange-yellow to a more lemon-yellow tint. It is thus possible to pass gradually, or 'continuously' so to speak, from perfectly clear to almost opaque colloidal solutions. Any one of these may be brought to the plait-point by adding alcohol and water in suitable

quantities, distribution becoming less as the clarity of the solution diminishes.

The distribution of arsenic and sulphur between the two phases has not yet been studied; it is possible that even when arsenious acid and hydrogen sulphide have been added in equivalent quantities the upper layer may contain more sulphur than is equivalent to the arsenic it contains. Nor has the effect (if measurable) of the sulphide on the composition of the system at the plait-point, or on the temperature at which a system of given composition becomes homogeneous, been determined. These matters, together with a quantitative investigation of the effect of hydrogen sulphide on the distribution ratios will be taken up in this laboratory during the coming winter.

Arsenic trisulphide, water, ether, acetone

The composition at the plait-point is about: water 4 cc, ether 5 cc, acetone 8 cc. Distribution was observed.

Arsenic trisulphide, water, ethyl acetate, alcohol

See Tables 1 and 2 and Fig. 1. Distribution may be observed here also, though not so readily as when ether is employed. The observations are interfered with by the saponification of the acetate, which may render a heterogeneous system homogeneous on standing.

Arsenic trisulphide, water, ethyl acetate, propyl alcohol

The composition at the plait-point is about: water 12 cc, ethyl acetate 5 cc, propyl alcohol 7 cc. Distribution was observed.

Antimony trisulphide, water, ether, alcohol

A dilute solution of tartar emetic was substituted for the arsenious acid. Distribution was observed; after a few days the upper layer had become colorless, and finally all the antimony sulphide subsided from both layers.

Antimony trisulphide, water, chloroform, alcohol

No distribution was observed; the sulphide remains in the upper layer as is the case with arsenious sulphide. We

intend to carry out similar experiments with benzene, carbon disulphide, etc., to see whether these substances resemble chloroform from this point of view.

Copper sulphide, water, ether, alcohol

A very dilute solution of copper acetate was used in place of the arsenious acid. No distribution was observed, the sulphide remaining in the lower layer although the plait-point was approached very closely. This agrees with Linder and Picton's opinion that colloidal solutions of copper sulphide are much further removed from the state of 'true' solution than are those of arsenious sulphide.

Summary

The occurrence of distribution of colloids between two immiscible solvents is not *a priori* impossible either from the point of view of the phase rule or from that of the electrified suspension theory of colloidal solutions. It may probably be easiest observed in the case of colloids with marked power of diffusion, and "immiscible solvents" which approach each other closely in properties and composition such as those near the 'critical solution temperature' in two component systems, or the solutions at the plait-point of the binodal curve in three component systems.

The Winkelblech effect interferes with the observation of such cases of equilibrium, for instance in the case of silver hydrosol and phenol, amyl alcohol, or isobutyl alcohol. Two experiments show the dependence of the Winkelblech effect on capillary forces.

Chloroform and alcohol do not coagulate the hydrosol of arsenious sulphide; but no distribution was observed even at the plait-point; this is not due to 'passive resistance.' The same is true when the alcohol is replaced by acetone; but if ether or ethyl acetate be substituted for the chloroform distribution readily occurs, whether the consolute liquid be alcohol, acetone, or propyl alcohol.

In this connection a rapid method of approximately

determining the binodal curve, tie-lines, and plait-point is described.

Antimony trisulphide, like the sulphide of arsenic, distributes between the two liquid phases in the system water-ether-alcohol, but not in the system water-chloroform-alcohol.

Copper sulphide does not distribute in the system water-ether-alcohol.

TABLE 1

Binodal Curves, Room Temperature

Water cc	Chloroform cc	Alcohol cc	Ether cc	Alcohol cc	Ethyl acetate cc	Alcohol cc
9.5	0.5	6.3	—	—	—	—
9	1	7.7	—	—	1	1.2
8	2	8.7	2	3.5	2	2.7
7	3	9.4	3	4.2	3	3.1
6	4	9.8	4	4.4	4	3.05
5	5	9.9	5	4.4	5	3.1
4	6	10.0	6	4.2	6	2.9
3	7	9.4	7	4.0	7	2.7
2	8	8.2	8	3.5	8	2.2
1	9	6.0	9	2.4	9	1.4

TABLE 2

Tie-Lines

Water, 6.5 cc; Chl., 3.5 cc			Water, 5 cc; Ether, 5 cc			Water, 5.5 cc; Et. acet., 4.5 cc		
Alcohol cc	Lower cc	Upper cc	Alcohol cc	Lower cc	Upper cc	Alcohol cc	Lower cc	Upper cc
8.4	8.5	9.7	2.0	6.6	5.0	2.5	6.7	5.6
9.0	9.0	9.7	2.5	6.8	5.2	3.0	6.9	5.9
9.4	9.7	9.4	3.5	7.6	5.3	—	—	—
—	—	—	4.0	8.3	5.0	—	—	—

The University of Toronto,
June, 1908.

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No. 84: SOME ESTERS OF ANTIMONY TRIOXIDE, BY JOHN FRANCIS MACKEY

(REPRINTED FROM THE TRANSACTIONS OF THE CHEMICAL SOCIETY, VOL. XCV)

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SOME ESTERS OF ANTIMONY TRIOXIDE.

BY

JOHN FRANCIS MacKEY.

From the Transactions of the Chemical Society, 1909. Vol. 95.

LXXVII.—*Some Esters of Antimony Trioxide.*

By John Francis MacKey.

In a previous paper, Lang, MacKey, and Gortner (Trans., 1908, **93**, 1364) described a method for the esterification of arsenious oxide with the fatty alcohols and with phenol and its homologues by removing the water produced by the reaction:

$$6ROH + As_2O_3 = 2R_3AsO_3 + 3H_2O$$

as quickly as it was formed by means of anhydrous copper sulphate placed in a Soxhlet tube attached to a flask containing weighed quantities of the reacting substances. By this means a large number of esters, which other methods had failed to produce, were prepared in quantity, and found to correspond with the general formula R_3AsO_3. In the present work, attempts were made to form the corresponding esters of antimony by five different methods, namely: (1) heating a mixture of the alcohol and antimony trioxide in a flask to which a reflux condenser was

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tities of the various alcohols were mixed with antimony trioxide and a considerable amount of anhydrous copper sulphate. The mixture was then placed in a shaking machine for three days at room temperature. In the case of *iso*butyl and *iso*amyl alcohols, esters were formed, but not in quantities sufficient to enable them to be isolated.

(iv) *Heating with Soxhlet attachment and anhydrous copper sulphate.*—Thirty grams of antimony trioxide were added to 160 grams of *iso*amyl alcohol in a 250 c.c. flask. An ordinary Soxhlet tube was connected with the flask, and a condenser, fitted with a calcium chloride tube, attached to the Soxhlet, which contained a large filter paper filled with anhydrous copper sulphate; the mixture in the flask was heated to boiling, and the water formed by the reaction was absorbed by the copper sulphate, which turned blue as soon as the first drops of condensed liquid fell on it. Heating was continued for about fifteen hours; after cooling, the clear product was poured off from the antimony trioxide and fractionated under diminished pressure. About 10·8 grams of the ester were formed, representing a yield of 13·62 per cent.

By this method esters were formed with methyl, ethyl, propyl, *iso*butyl, amyl, and *iso*amyl alcohols, as shown in the following table:

Table of yields by various methods.

Ester.	Reflux condenser.	In sealed tubes.	Anhydrous copper sulphate. In the cold.	Anhydrous copper sulphate. In Soxhlet.
Methyl	nil	nil	nil	8·09 per cent.
Ethyl	,,	,,	,,	3·00* ,,
Propyl	,,	,,	,,	13·3 ,,
*iso*Butyl	trace	,,	trace	15·11 ,,
Amyl	nil	,,	nil	13·16 ,,
*iso*Amyl	trace	,,	trace	13·62 ,,

* It will be noticed that the same extremely low yield of ester with ethyl alcohol occurred in the preparation of the esters of arsenious acid, described in a former paper, where a possible explanation was advanced.

These esters were purified and analysed, the following methods of analysis being employed.

Method of analysis for esters of the aliphatic alcohols (using iso*amyl antimonite as an example*).—Two methods were employed for the determination of the antimony. In the first method, iodine was used to oxidise the trioxide to the pentoxide, but was not found to give accurate results, so that the following procedure was adopted.

1·0057 Grams of the ester were decomposed by 5 c.c. of concentrated hydrochloric acid, 50 c.c. of tartaric acid solution were

added, and the antimony was precipitated from this solution by means of hydrogen sulphide; the antimony sulphide thus formed was converted into antimony tetroxide by treatment with fuming nitric acid and ignited:

1·0057 gave 0·4024 Sb_2O_4. Sb = 31·57.

$C_{15}H_{33}O_3Sb$ requires Sb = 31·48 per cent.

This method of analysis gave the following results:

Ester.	Percentage of Sb found.	Percentage of Sb calculated from the formula R_3SbO_3.
Methyl	56·68	56·41
Ethyl	—	47·41
Propyl	40·29	40·40
*iso*Butyl	35·37	35·40
Amyl	31·44	31·48
*iso*Amyl	31·34	31·48

Expressing these as salts of antimonous acid, we arrive at the general formula R_3SbO_3 for them.

Properties of the Esters of the Aliphatic Alcohols with Antimony Trioxide.

Methyl antimonite is a colourless liquid, b. p. 65°, sp. gr. 1·025.

Ethyl antimonite is a colourless liquid, b. p. 115—120°.

Propyl antimonite is a yellow liquid, sp. gr. 1·042, b. p. 143°/30 mm.; at atmospheric pressure it decomposes into propyl alcohol and antimony trioxide at 200°.

iso*Butyl antimonite* is a yellow, mobile liquid, sp. gr. 1·058, b. p. 144°/30 mm.; it decomposes into *iso*butyl alcohol and antimony trioxide at 250° under atmospheric pressure.

Amyl antimonite is a yellow liquid, sp. gr. 1·079, b. p. 170°/30 mm.

iso*Amyl antimonite* is a yellow, mobile liquid, sp. gr. 1·081, b. p. 163°/30 mm.; at 250°, under atmospheric pressure, it decomposes into antimony trioxide and *iso*amyl alcohol.

All these esters are readily soluble in absolute alcohol, ether, chloroform, or benzene, but decompose immediately on addition of water into antimony trioxide and the alcohol from which they were prepared.

The fifth method was not employed for the aliphatic alcohols.

Esters obtained with Phenol and its Homologues.

For the esterification of these substances with antimony trioxide, two method were used, namely, heating the mixture of phenol and antimony trioxide in a flask to which a Soxhlet apparatus

containing anhydrous copper sulphate was attached, and heating the mixture of phenol and antimony trioxide with calcium turnings in a flask under a reflux condenser. By these means esters were obtained with phenol, *o*-, *m*-, and *p*-cresols. In the case of phenol and *m*-cresol, unsuccessful attempts to obtain the esters were made by heating these materials with antimony trioxide with a reflux condenser only.

Phenyl antimonite.—One hundred and twenty-five grams of phenol and 25 grams of antimony trioxide were heated in a flask fitted with a Soxhlet apparatus containing anhydrous copper sulphate. Clouds of steam began to form at 100°, indicating that the reaction began at that temperature; the thermometer rose very quickly to the boiling point of phenol, and remained very close to that temperature (varying from 170° to 180°) for about seven hours, when the temperature gradually rose, and, after fifteen hours' heating, reached a maximum of 290°. This maximum is the highest temperature to which the ester can be heated without decomposition. The mixture of phenol, ester, and antimony trioxide was then shaken with water-free benzene, causing the precipitation of the antimony trioxide dissolved in the ester and in the phenol, and, after filtering, fractionated under diminished pressure. The benzene distilled at 30°, phenol at 70°, and the ester at 250°.* The ester was purified by dissolving in benzene, filtering from any antimony trioxide, and separating by passing a current of hot, dry air over the benzene solution placed in a vacuum desiccator. The crystals thus obtained had no very definite melting point owing to the presence of some phenol. To remove the latter, the crystals were heated to 200° for twenty minutes, dissolved in benzene, filtered, and crystallised as before. The crystals thus obtained were light brown in colour, and melted at 13°. At 18°, *phenyl antimonite* has a specific gravity of 1·621, and boils at 250°/30 mm. It dissolves readily in absolute alcohol, ether, chloroform, or benzene, and decomposes on addition of water into phenol and antimony trioxide. On analysis, it was found to correspond with the formula $(C_6H_5)_3SbO_3$ or $(C_6H_5O)_3Sb$. This ester was also prepared by heating a mixture of phenol, antimony trioxide, and calcium turnings in a flask fitted with a reflux condenser. By this method, a yield of 62 per cent. was obtained after two hours' heating. By the former method the yield is not more than 40 per cent. after fifteen hours' heating.

o-, m-, and p-*Tolyl Antimonites.*—One hundred and fifty grams of each of the cresols were heated with about 30 grams of antimony trioxide, using the methods described above. The excess of

* Even at 250° the ester suffers partial decomposition.

antimony trioxide was separated by means of benzene, filtered, and the esters fractionated. After purification they were analysed, and found to correspond with the formula $(C_6H_4{\cdot}CH_3)_3SbO_3$ or $(C_6H_4{\cdot}CH_3{\cdot}O)_3Sb$. o-*Tolyl antimonite* crystallises in dark brown masses, and melts at 16°; its specific gravity is 1·480, and it boils at 352°. m-*Tolyl antimonite* is a yellow liquid, with a specific gravity of 1·475, and boils at 300°/30 mm. p-*Tolyl antimonite* is a dark brown, crystalline solid, melts at 14°, has a specific gravity of 1·495, and boils at 345°/30 mm.

Whilst in the case of the aliphatic alcohols a drying agent in the Soxhlet apparatus was essential to absorb the water formed and allow the alcohols only to drop back into the mixture, no drying agent was necessary with the phenols, as practically no phenol or ester ever found its way further than the side-tube of the Soxhlet.

The water formed remained in the Soxhlet, there being never sufficient volume of water produced to cause the syphon attachment to come into play. The use of metallic calcium, it will be noticed, gave a better yield of ester than the Soxhlet method.

Method of Analysis of Phenyl and Tolyl Esters.—To 1·5960 grams of phenyl antimonite, 5 c.c. of potassium hydroxide (containing 7 grams per 10 c.c.) were added, and then an excess of tartaric acid. The excess of tartaric acid was neutralised by sodium carbonate, and 25 c.c. of sodium hydrogen carbonate added. The whole was diluted to 500 c.c., and two samples of 20 c.c. each were taken for analysis. To each, 20 c.c. standard iodine was added in excess (shown by the formation of a precipitate of tri-iodophenol and the appearance of a clear yellow solution), the temperature being kept at 65°. The mixture was then cooled, acidified with dilute sulphuric acid, and diluted with water to 500 c.c. The tri-iodophenol was filtered off, and the excess of iodine in 100 c.c. of the filtrate was titrated against standard thiosulphate, using starch as indicator. The quantity of thiosulphate necessary, multiplied by five, represents the quantity of iodine that was in excess. This quantity, subtracted from the original amount of the iodine added, gave the amount necessary to change both the phenol to tri-iodophenol and the antimony trioxide to antimony pentoxide.

Owing to the presence of tartaric acid in the above, it was impossible to estimate at all accurately the antimony trioxide by means of dichromate. The method previously described under *iso*amyl antimonite, namely, weighing the antimony as antimony tetroxide, was used. The percentage of antimony, as determined in this way, was found to be 30·10. The strength of the iodine

being known, the number of c.c. of iodine equivalent to 30·10 per cent. of antimony was subtracted from the iodine obtained in the previous determination, the difference being the amount combined with phenol.

To test the accuracy of this method, estimations were made with weighed quantities of (*a*) phenol, (*b*) antimony trioxide, (*c*) a mixture of these.

(*a*) To 0·8826 gram of phenol, 5 c.c. of a solution of potassium hydroxide (7 grams per 10 c.c.) were added, and the whole diluted with water to 250 c.c. ... ... (1)

10 c.c. of this solution were equivalent to 28·90 c.c. of iodine.

(*b*) To 0·5000 gram of antimony trioxide were added 25 c.c. of a saturated solution of tartaric acid; sufficient sodium carbonate to neutralise the excess of the tartaric acid and 50 c.c. of sodium hydrogen carbonate were then added, and the whole diluted with water to 500 c.c. ... ... (2)

100 c.c. of this solution were equal to 13·70 c.c. of iodine.

(*c*) To 10 c.c. of (1) were added 100 c.c. of (2), and together required 42·45 c.c. of iodine.

Thus 100 c.c. of (2) required 13·70 c.c. of iodine, and 100 c.c. of (1) required 28·90 c.c. of iodine; in all, 42·60 c.c., as compared with 42·45 c.c. when mixed, a difference of less than one-third of 1 per cent., which is well within the limits of experimental error.

Properties of the Esters of Phenol and its Homologues.

	Phenyl.	*o*-Tolyl.	*m*-Tolyl.	*p*-Tolyl.
Percentage yield	40·0	48·2	48·3	40·8
B. p./30 mm.....	250°	352°	300°	345°
Sp. gr.	1·621	1·480	1·475	1·495
M. p.	13°	16°	—	14°

The preparation of other esters from the oxides of arsenic and antimony and compounds containing alcoholic hydroxyl is being proceeded with in this laboratory. Attempts are also being made to overcome the difficulties experienced in obtaining the esters of sulphoarsenious acid in sufficient quantities to allow of their compositions being determined.

I wish to express my thanks to Professor W. R. Lang for suggesting this research, and for the interest he has taken in the work.

CHEMICAL LABORATORY,
UNIVERSITY OF TORONTO.

R. CLAY AND SONS, LTD., BREAD ST. HILL, E.C., AND BUNGAY, SUFFOLK.

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UNIVERSITY OF TORONTO STUDIES

PAPERS FROM THE CHEMICAL LABORATORIES

No. 85: HARCOURT AND ESSON'S IDEA IN CHEMICAL MECHANICS, BY W. LASH MILLER

(REPRINTED FROM TRANSACTIONS OF THE ROYAL SOCIETY OF CANADA, 3RD SERIES, VOL. II)

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XXI—*Researches in Physical Chemistry carried out in the University of Toronto during the past year.*

Communicated by PROFESSOR W. LASH MILLER.

(Read May 27, 1908.)

1. H. C. COOKE:—*The condensation of oxalic and acetic esters by sodium ethylate.* The study of the effects of conditions on the red colouration given by ferric chloride with the condensation product has been continued, and a number of measurements of the rate of condensation have been made.

2. S. DUSHMAN:—*The behaviour of copper as anode in solutions of chlorides* (read before the American Electrochemical Society). The experiments are in quantitative accord with the hypothesis that at the anode there is chemical equilibrium between metallic copper and the cuprous and cupric salts in solution.

3. R. A. GORTNER:—*The kinetics of the reaction between chromic and hydriodic acids and ferrous salts.* Miss Benson's experiments at high temperatures were extended; while increase of temperature retards the liberation of iodine, it accelerates the oxidation of the ferrous salt. Fluorides, bromides and chlorides retard the rate of liberation of iodine in the order named, they accelerate the oxidation of the ferrous salt. The effect of 'ageing' on the ferric salt is altogether due to hydrolysis. In some of the experiments hydrochloric acid was substituted for sulphuric. (Published in The Journal of Physical Chemistry).

4. H. C. GRAHAM:—*Direct determination of the transport number of acetic acid.* Mr. Dawson's experiments were continued; an attempt was made to eliminate the effect of diffusion by choosing the concentrations of chromic acid and copper acetate, so that the acetic acid generated at the two boundaries might have the same concentration.

5. R. J. MANNING:—*Physico-chemical study of Tannin.* The solutions in water show a well marked rise in boiling point over that of pure water even before hydrolysis into [illegible] gallic acid takes place. They show no Tyndall effect, and give measurable osmotic pressures with gelatine membranes. The distribution of tannin between water and ether, water and ethylacetate, and water and amylalcohol was determined; in the case of ether the ratio is independent of the concentrations. As a result of these measurements tannin can hardly longer be considered to be a colloid.

   The marked effect of traces of water on the solubility of tannin and of other glucosides in organic solvents was also studied.

6. W. LASH MILLER:—*Indirect analysis by means of the dilatometer.* A method of determining the composition of one of the phases at a transition point, without isolating or analysing it. (Published in The Journal of Physical Chemistry.)

7. H. P. MILLS:—*The chromic acid electrode.* The E. M. F. of the hydrogen electrode in chromic acid is found to be dependent on the rate of diffusion of hydrogen to the platinum and on the (much quicker) rate of reduction of the chromic acid by the hydrogen at the platinum surface.

In this connection the rate of reduction of chromic acid by hydrogen in presence of colloidal platinum has been measured; it seems to depend only on the rate of diffusion of the dissolved hydrogen to the particles of platinum in the suspension.

8. A. F. ODELL:—*The condensation of oxalic ester with acetophenone.* By means of special apparatus the yield of the condensation product was determined, to test Claisen's hypothesis of equilibrium. The experiments are not yet finished.

9. L. V. REDMAN:—*The electrolysis of copper sulphate in sulphuric acid solutions with interrupted and alternating currents.* The results of the experiments with interrupted currents show that the relative amounts of hydrogen and copper liberated at the cathode depend on diffusion, and cannot be accounted for by Siegrist's hypothesis of reaction velocities.

10. R. B. STEWART:—*The Hydrogen electrode in acetic acid.* The experiments shew that the electrode is reversible; and a special apparatus has been constructed to determine the transport number of acetic acid by measuring the E. M. F. of concentration cells.

XXII.—*Harcourt and Esson's Idea in Chemical Mechanics.*

By W. LASH MILLER.

(Read May 27, 1908.)

I think that I will make the best of the limited time at my disposal by defining at once the fundamental problem of chemical kinetics, for it is with the rates of chemical change that I propose to deal. This problem is, then, to find how the rate of a chemical reaction depends on the circumstances under which that reaction takes place; and in the simple case with which alone we shall be concerned, the simple case that the reaction takes place in a homogeneous solution, the only circumstances that affect the rate are:—the temperature, and the concentrations of the chemicals in the solution.

The kindness of those in charge of this laboratory puts me in the position to illustrate what I say by a concrete case. Here are samples of the very chemicals used by Harcourt and Esson in their experiments forty years ago;[1] a solution of oxalic acid, water, sulphuric acid, and a solution of potassium permanganate. When these are mixed together, the whole solution looks pink from the presence of the permanganate; on standing awhile, however, the colour will gradually fade, owing to the reduction, or destruction, of the red permanganate; and what is meant by the "rate" of the reaction is the number of grammes of permanganate that are reduced, or destroyed, or fade per second.

That this rate depends on the temperature, may easily be seen if I pour a little of the mixture into a test-tube and heat it over the flame. As the solution gets warmer, the colour fades more rapidly, until now it is all gone, while the part left at the temperature of the room is still deep red.

The rate depends also on the concentrations of the chemicals dissolved in the solution; so that

Rate depends on a, b, c, d, ...t

and the fundamental problem of chemical kinetics is to determine quantitatively the relation between the rate, the concentrations and the temperature.

Now for the fundamental difficulty. This lies in the fact that as the reaction proceeds, the temperature changes, owing to the liberation or absorption of heat by the reaction; and the various concentrations on

[1] Jour. Chem. Soc., *20* 460 (1866).

which also the rate depends, also change, those of the reacting substances growing smaller, and those of the products of the reaction growing greater.

Thus, as all these circumstances, on which the rate depends, keep changing during the reaction, the rate itself must keep changing throughout the very experiment we are making to study it. This is the fundamental difficulty of experiments in chemical kinetics.

Now as to the way in which this difficulty is overcome; and first as to the temperature. That is kept constant during the experiment very simply by placing the beaker in a large tub of water kept at constant temperature,—a thermostat, as it is called. After determining the rate at one temperature, the solutions and the thermostat are warmed up to some other temperature, and the experiment is repeated, all the concentrations and everything but the temperature being the same, thus the influence of the temperature is ascertained. In cases where it is not possible to hold the temperature constant during an experiment—as in the study of explosions, for instance—it is much more difficult to interpret the results of the experiments, and the study of those reactions is much less advanced than that of those where a thermostat can be employed.

So much for the temperature; it is kept constant during the experiment, and the rates in experiments at different temperatures are compared. Now for the concentrations. Can they too be kept constant during the reaction? No one has yet invented a concentrationstat, so far as I am aware; but as Harcourt and Esson pointed out, the concentrations will not change *much* during the experiment, if the quantities of chemicals put into the beaker are large compared to the quantities of the same chemicals formed or destroyed during the reaction. Now, that is what I did in this beaker; there is very nearly as much oxalic acid and sulphuric acid here yet as there was before the permanganate was added, because the amounts of those two substances put in in the first place were much greater than would react with the permanganate used. The concentrations of oxalic acid, and sulphuric acid, therefore have remained practically constant during the experiment, and the temperature would have, if the beaker had been stood in a tub.

This is the way Harcourt and Esson worked, and I may express these conditions on the board[1] by writing large letters for B, C, etc., the concentrations of the reagents of which relatively large quantities were used, and a little "a" for the permanganate. B, C, etc., stay constant, because they are large, and perhaps it will not confuse if I write a large T

[1] See table, p. 248.

for the temperature, to indicate, not that it was very hot, but that that factor too was kept constant (by the use of a thermostat).

The concentration of the permanganate, of course, changed during the experiment, we saw it fade away; the rate too changed; but as the change in the rate was caused only by change in the concentration of one of the reagents, it was a relatively easy matter for Harcourt and Esson to discover the relation between the rate and the concentration of that one substance; the effect of the concentrations of the others was determined like that of the temperature, by comparing different experiments in which these concentrations were different, while remaining constant throughout each.

This method of working is the "idea" of which I spoke. It may, perhaps, seem a very obvious idea, and hardly worth while making a fuss about; and, indeed, Harcourt and Esson seem to have considered it so. But it is true, although to those who are not familiar with this branch, it may seem difficult to believe, that even now—forty years after the publication of Harcourt's experiments—this method is not in general use, and that for thirty-six years it was never used at all and practically all experiments on the rates of chemical reactions were carried out in solutions in which the concentrations of all the chemicals varied greatly during the experiments.

In reply to the question "How is it possible to find the connection between rate and concentrations from experiments so badly planned as these," the answer is "By the method of guess and try." Make some plausible assumption, express it mathematically, and compare the experiments with the methematical deductions from the assumption, or guess. If they agree, well and good. If they don't, guess again. The trouble is, that in case of a bad guess the experiments themselves don't give much help in making a better.

This method, then, I shall call "the Method of Guess and Try," in contradistinction to Harcourt and Esson's method of "Systematic Exploration."

Of course, there are connecting links. Two of the concentrations, for instance, may be small, and the others large; the effect of the former being arrived at by guess and try, and that of the latter by systematic exploration. Hood [1] used such a half-and-half method in 1878.

With regard to the method of guess and try; it is hard to teach people how to guess,—that is "chemical instinct;" but van't Hoff, in his celebrated "Études" [2] or "Studies on Chemical Dynamics,"

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[1] Phil. Mag. (5) 6 371 (1878).

[2] Etudes de dynamique chimique, 1884, p. 87.

distinguished two ways of trying, or testing the assumptions by experiment. I shall not enlarge on these further than to say that the better way, the sharper test, involved comparing experiments in which the initial concentrations of the chemicals were varied, while the other relied altogether on the results of a series of analyses of the same solution at different intervals of time. The first of these methods was used by van't Hoff in his book, the other, exclusively, by his successors, for twelve years.

To resume, then, there are shown in this table four ways of determining the relation between the rate of a chemical reaction and the concentrations. Systematic exploration, Harcourt and Esson, 1866; a hybrid method, 1878; and the method of guess and try, with two ways of trying, of which the better was used by van't Hoff in 1884, and the other was in general use between 1884 and 1895.

Method.	Definition.	Used by
1. Systematic Exploration—Harcourt & Esson's.....	a, B, C, D, ...T	H and E, 1866
2. Hybrid	a, b, C, D, ...T	Hood, 1878
Guess and Try.....	a, b, c, d, ...T	
3. (a) varying initial conc's.....	.....	van't Hoff, 1884
4. (b) varying time only.....	.....	General, 1885-1895
5. The logical extreme.....	a, b, c, d, ...t	Not employed

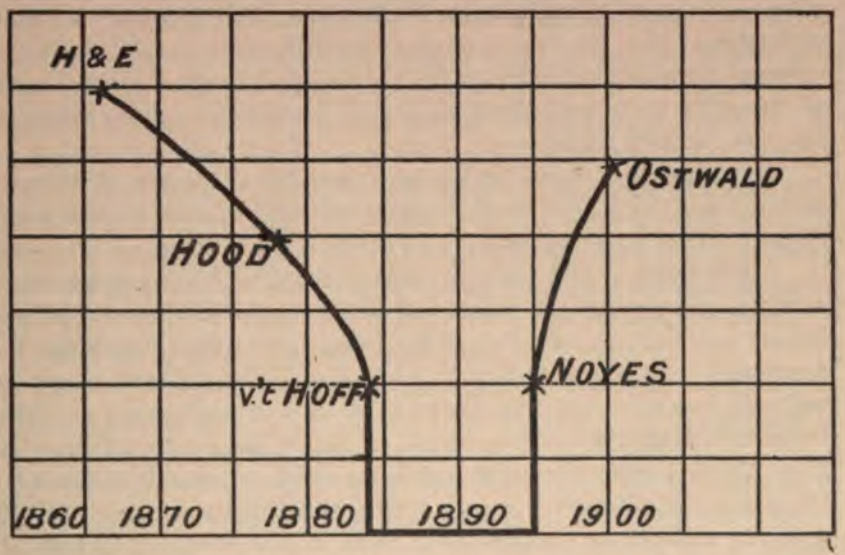
I should like to put all this in a diagram; that will make it look more like physical chemistry. The only trouble is what co-ordinates to use. The dates will do for the abscissæ, that's obvious, and I will put Harcourt and Esson high up, because the method they employed was the one best adapted for the purposes of discovery, and Hood a little further down, and then van't Hoff, with the method of varied initial concentrations, and then all the chemists from 1885 to 1895. So that the abscissæ are chronological, and the ordinates psychological.

I would not like to give the impression that van't Hoff, for instance, used a method that was unsuitable for the purpose he had in hand. He had a definite object, and his method enabled him to attain it. In Hood's case, too, there was a special reason—not a very good one, perhaps—that kept him from using method number one; and he too got all he wanted with number two. But the fact is plain, that as time went on,

weaker and weaker tools were coming into use, until the very recollection of the method of Harcourt seems to have died out.

If there were time, I should like to go into the reasons for this gradual adoption of the methods of guess and try, but there isn't. It is connected, however, with Guldberg and Waage's application of the kinetic theory to this subject, which made men feel that they were likely to be good guessers. They thought they had a sure tip.

This short line on the board[1] represents ten years of active work, the *Zeitschrift für physikalische Chemie* was founded here, and Arrhenius' theory of electrolytic dissociation was first applied to a kinetic problem here. Dozens of reactions were studied from the kinetic point of view,



all by method number four; and with the result that might be predicted. If the case experimented with happened to be a simple one, the law was guessed; if not, it wasn't. And so, in addition to the reactions for which the relations between rate and concentrations were ascertained, there were gradually being discovered a number of reactions for which these relations could not be formulated.

The first step upward was taken in 1895, by Dr. now Professor A. A. Noyes.[2] He reintroduced van't Hoff's method, method three; quoted van't Hoff's arguments to show that it is superior to number four; and proved its superiority by recalculating Magnanini's measurements (Mag-

[1] Referring to diagram.
[2] Zeit. phys. Chem., *18* 119 (1895).

nanini's work comes here, 1891), and finding quantitative relations where the latter had seen none. Noyes used this method number three in his own work, and discovered the first reactions of the third order studied since the time of Hood.

The next incident is the appearance of the second edition of Ostwald's Lehrbuch, or rather of the second edition of vol. 2, part 2, Heft 2, with the chapter on kinetics. In this, after reviewing the methods of working in common use, viz.: methods three and four of our classification, Ostwald suggests working with all the chemicals but one in excess, and determining the effect of that one on the rate—Harcourt's method, so far. Harcourt's name is not mentioned at all in this connection, however, and reading a little further shows that it is not Harcourt's method after all; because when it comes to determining the effect of the concentration of B on the rate, instead of preparing the experiments with a different excess of B, it is proposed to make b small in turn, and so with all, one after the other. The method used in Harcourt's paper seems to have been quite forgotten.

When planning work for the laboratory for the winter of 1902, I read this new method of Ostwald's with the greatest interest, and fully appreciated the advantages set out so clearly by the author.

On thinking over the case in which I was specially interested, however (the reaction between chloric and hydriodic acids in presence of free iodine) I found that the effect of the iodine concentration could not be ascertained by this new method; to ascertain it, it would be necessary to make up a solution, in which the concentration of the iodide was much lower than that of the others, including that of the iodine. Now, it is impossible to prepare a solution containing much iodine and little iodide, the iodine won't dissolve. And on further thought, I saw that my object could be attained by comparing the rates in two solutions, in both of which the iodide was in excess, but different excesses. The method of Harcourt again, at last.

I didn't know it was Harcourt's at first; in fact, it was only in the winter, when the work was well advanced, that in connection with some work that Mr. Bell[1] was doing, I had occasion to read Harcourt's paper, and found what I had begun to regard as *my* method clearly described.

This tool once in our hands, it is not surprising that we should be able to solve problems that had proved too much for some of the best known chemists working under less favourable circumstances.

The rates of oxidation of hydriodic acid, for instance, by the oxy-

[1] Jour. Phys. Chem., 7, 61 (1903).

acids of the halogens, had been studied by Burchard [2] in the laboratory of Lothar Meyer, by Ostwald,[3] by Meyerhoffer,[4] by Dr. Schlundt [5] in Wisconsin, by Warder,[6] of Washington, by Magnanini [7] in Italy, and by Pendlebury and Seward,[8] and Judson and Walker [9] in England. Most light had been thrown on the reaction by Prof. Noyes;[10] but in the opinion of the last chemists to work on this subject, Messrs. Judson and Walker, expressed in 1898 after a review of the earlier papers: "The action of hydriodic acid on the oxyacids of the halogens is of too intricate a nature to give any satisfactory numerical results."

Attacked by the method of systematic exploration, however, this problem proved easy of solution; Messrs. Bray,[11] Dushman [12] and Clark[13] expressed the relations between concentrations and rate in mathematical form, traced out the influence of the iodine liberated during the reaction, and recalculated most of the experimental work of their predecessors. The remarkable catalytic action of chromic acid on one of these reactions, discovered by Ostwald, has also been studied in detail.[14]

In this connection, it became apparent that reactions of the fourth order are plentiful as blackberries in August; and in the oxidation of ferrous salts by chromic acid, Miss Benson[15] found one of the fifth. The opinion held between 1884 and 1895, that reactions of a higher order than the second are curios, must, therefore, be given up. It probably arose from the circumstance that the method of investigation employed was unable to cope with the complicated cases.

Some of these results might conceivably have been attained by a judicious use of method number three. It is otherwise with the reactions to which I will now refer.

Schwicker,[16] who studied the formation of iodate by the action of iodine on caustic potash in 1895, thought that he had discovered a re-

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[2] Zeit. phys. Chem., *2*, 796 (1888).
[3] Zeit. phys. Chem., *2*, 127 (1888).
[4] Zeit. phys. Chem., *2*, 585 (1888).
[5] Am. Chem. Jour. *17*, 754 (1895).
[6] Am. Chem. Jour. *18*, 23 (1896).
[7] Gazz. Chim. Ital., *21*, 476 (1891).
[8] Proc. Roy. Soc., *45*, 396 (1889).
[9] Jour Chem. Soc., *73*, 411 (1898).
[10] Zeit. phys. Chem., *19*, 599 (1896).
[11] Jour. Phys. Chem., 7, 92 (1903).
[12] Jour. Phys. Chem., *8*, 453 (1904).
[13] Jour. Phys. Chem., *10*, 679 (1906).
[14] Jour. Phys. Chem., *11*, 353 (1907).
[15] Jour. Phys. Chem., 7, 1 (1903).
[16] Zeit. phys. Chem., *16*, 303 (1895).

action of the third order; Noyes[17] showed by a recalculation based on method three, that under some circumstances, at least, it is of the first. Mr. Forster,[18] who subjected the reaction to a "systematic exploration," showed it had no "order" at all; that the effect of increasing the concentration of the potash was first to increase and then to decrease the rate. The relations found by Forster had not been guessed by his predecessors, and, consequently, were not revealed by their method of working.

The last reactions of which I shall speak, are the reactions grouped under the common name "induction." Here, two reactions take place in the solution at once, and the rates of each are affected by the concentrations of four or more chemicals.[19] The experimental study of complicated cases like these is, to put it shortly, absolutely impossible by any method other than that which I have called "systematic exploration." Guess and Try is no good; not that one can't guess—some people, I don't know whether any chemists among them, are able to guess the result of a horse race, or of a flurry in stocks—but the "trying" needs the systematic procedure.

Manchot,[20] Schilow, and Luther[21] guessed at the mechanism of the induction by iron of the reaction between chromic acid and hydrogen iodide. Miss Benson's experiments[22] showed that they guessed wrong; and a long series of experiments by Mr. DeLury[23] on the induction of the same reaction by arsenious acid, furnish the first proven case of induction according to the peroxide formula. No other cases of induction have been studied from this point of view; and no others can be, except by this method.

Working with this tool of Harcourt's, we have been able to sharpen it a little, and extend its usefulness. Without going into details, it was obviously only a short step to pass to the "method of constant rates,"[24] in which all the concentrations, and rates as well, are kept constant during the experiments.

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[17] Zeit. phys. Chem., *18*, 129 (1895).

[18] Jour. Phys. Chem., 7, 640 (1903).

[19] Jour. Phys. Chem., *11*, 9 (1907).

[20] Liebig's Annalen, *325*, 95 (1902).

[21] Zeit. phys. Chem., *46*, 777 (1903).

[22] Jour. Phys. Chem., 7, 356 (1903).

[23] Jour. Phys. Chem., *11*, 54 (1907).

[24] Jour. Phys. Chem., 7, 92 (1903).

Method.	Definition.	Used by
Systematic Exploration:—		
Method of Constant Rates...	A, B, C, D, ...T	Bray 1902
Harcourt & Esson's.....	a, B, C, D, ...T	H and E, 1866

This method has proved serviceable in some of the more complicated cases, where even Harcourt's method was none too good.

Then, in some special cases, a way has been found of keeping a concentration constant without using excess of the constituent;[25] and most valuable of all, perhaps, it has been found possible to apply Harcourt's principles to the study of chemical equilibrium. The equilibrium, in solutions containing iodine, iodide, acid, arsenite, and arsenate, is (so far as I know) the most complicated yet studied; Mr. Roebuck [26] cleared the whole matter up in a few weeks by the application of a method analogous to No. 1 of our table.

I am very glad to have been afforded this opportunity, more than forty years after Harcourt and Esson's first publication, to offer this testimony to the value of the indispensable "idea" with which they have endowed the study of chemical mechanics. No stronger testimony could be offered of the power of the tool which they have placed in our hands, than the fact that young chemists, most of them just completing their college course, have attacked and solved problems which had been left unsolved by some of the most able workers of the present day.

And when I think of a review [27] of Harcourt and Esson's paper published in 1895, in which—after expressing pleasure that these pioneers had again returned to work in the old fields—the reviewer regretted that they had taken so little notice of the progress made since their last visit, I feel that these fathers of the science would have been justified in replying, if they had had an opportunity of replying—you can't reply to a reviewer—that so far as the method of working went, a great deal of the progress since 1866 had been made down hill.

[25] Jour. Phys. Chem., *8*, 454 (1904).
[26] Jour. Phys. Chem., *6*, 365 (1902).
[27] Zeit. phys. Chem., *19*, 177 (1906).

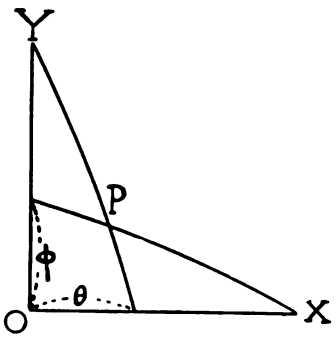
XXIII.—*An Outline of Analytical Spherical Geometry.*

By S. BEATTY, B.A.,

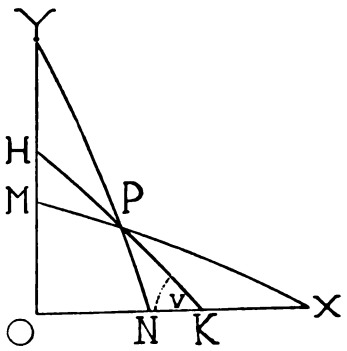
Fellow in Mathematics, University of Toronto.

(Presented by Professor Alfred Baker, and read May 26th, 1908.)

I. In analytical spherical geometry several systems of axes present themselves. The first to be considered is that analogous to the Cartesian in plane geometry. It will be subsequently noted that the great circle plays the same role in spherical geometry as the straight line in analytical plane geometry. Consequently, we choose as axes any two great circles passing through a fixed point O called the origin; much labour will be avoided if the axes are taken as making an angle of 90° at the origin. Furthermore, the lines OX and OY are each taken a quadrant in angular distance. The co-ordinates θ and ϕ of a point P are defined to be the angular intercepts on OX and OY made by the great circles YP and XP respectively. The following diagram makes clear the meaning intended. As in plane geometry the directions OK and OY are by convention positive. The reverse are negative.

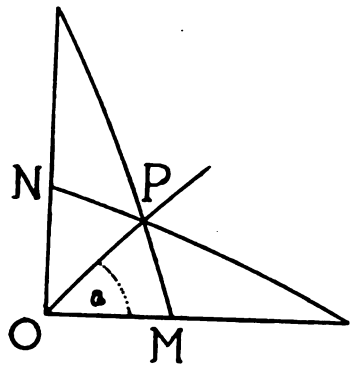


II. As has been intimated, the simplest curve on the surface of the sphere is the great circle. The equation in the case where the angular intercepts are α and β is readily found. From triangles NPK and NPX we have $\sin(\alpha - \theta) \tan V = \tan PN = \cos\theta \tan\phi$. But $\sin\alpha \tan V = \tan\beta$. On eliminating V the equation of the great circle, $\frac{\tan\theta}{\tan\alpha} + \frac{\tan\phi}{\tan\beta} = 1$, results.



III. This may become the equation of any great circle on the surface of the sphere by giving to α and β particular values, as long

as $O < |\alpha| < \pi$, with a similar relation for β. In the particular case where $\alpha = \beta = o$ the equation is readily obtained.



$\cos\theta \tan\phi = \tan PM = \sin\theta \tan a$ or $\tan\phi - \tan\theta \tan d = o$. This becomes $\tan\phi = m \tan\theta$ where $m = \tan a$. This has included the case where $\alpha = \beta = \pi$. Suppose, further, that $\alpha = O$ and $O < |\beta| < \pi$. This is readily seen to have as equation $\tan\theta = o$. When $\alpha \pm O$, and $\beta = \frac{\pi}{2}$ the equation is $\tan\theta = c$, which for different values of c may become any great circle passing through the poles of OX. We conclude, therefore, that in all cases the equation

$$A \tan\theta + B \tan\phi + C = o$$

represents a great circle; furthermore, all great circles are represented by this equation.

IV. It is interesting to note that if $a = \alpha R$, $b = \beta R$, $x = \theta R$, and $y = \phi R$ the equation

$$\frac{\tan\theta}{\tan\alpha} + \frac{\tan\phi}{\tan\beta} = 1,$$

as R becomes infinite, becomes the familiar equation in plane geometry,

$$\frac{x}{a} + \frac{y}{b} = 1.$$

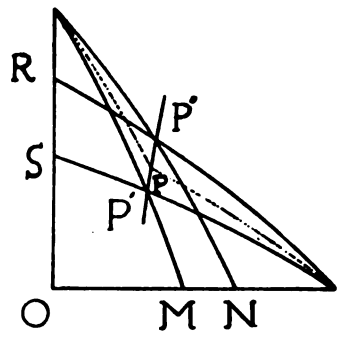
Similar remarks apply to the two type forms,

$$\begin{aligned} \tan\phi - m \tan\theta &= o \\ \tan\theta - c &= o. \end{aligned}$$

V. The fundamental equation of all great circles could be taken as

$$\begin{vmatrix} \tan\phi & \tan\theta & 1 \\ \tan\phi' & \tan\theta' & 1 \\ \tan\phi'' & \tan\theta'' & 1 \end{vmatrix} = o,$$

the circle being defined through the property that two points on it are given. The following analytic method would seem to give us this equation, from first principles. Suppose the equation of the circle through the points P' and P'' is required; let P be any point on this circle; suppose the co-ordinates of these points are in order $(\theta' \phi')$, $(\theta'' \phi'')$, and $(\theta \phi)$.



Then
$$\frac{\sin P'P}{\sin(\theta - \theta')} = \frac{\sin AP'}{\sin LP}$$
$$\frac{\sin(\theta'' - \theta)}{\sin P''P} = \frac{\sin LP}{\sin AP''}$$

That is
$$\frac{\sin P'P}{\sin P''P}\,\frac{\sin(\theta'' - \theta)}{\sin(\theta - \theta')} = \frac{\sin AP'}{\sin AP''} = \frac{\cos P'M}{\cos P''N}$$

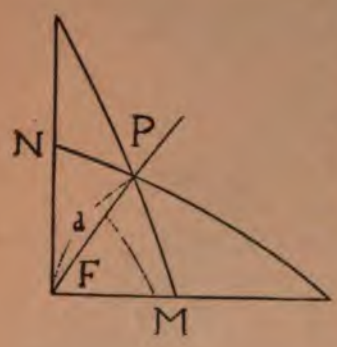
So too
$$\frac{\sin P''P}{\sin P'P}\,\frac{\sin(\phi - \phi')}{\sin(\phi'' - \phi)} = \frac{\cos P''R}{\cos P'S}$$

Therefore
$$\frac{\sin(\theta'' - \theta)\sin(\phi - \phi')}{\sin(\theta - \theta')\sin(\phi'' - \phi)} = \frac{\cos P'M \cos P''R}{\cos P''N \cos P'S} = \frac{\cos\phi' \cos\theta''}{\cos\theta' \cos\phi''} \cdot \frac{\cos\theta \cos\phi}{\cos\theta \cos\phi}$$

Therefore
$$\frac{(\tan\theta'' - \tan\theta)}{(\tan\theta - \tan\theta')} = \frac{(\tan\phi'' - \tan\theta)}{(\tan\phi - \tan\phi')}$$

Or
$$\frac{(\tan\theta - \tan\theta')}{(\tan\theta' - \tan\theta'')} = \frac{(\tan\phi - \tan\phi')}{(\tan\phi' - \tan\phi'')}$$

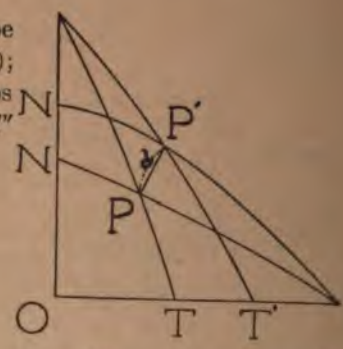
VII. Let us now proceed to find the angular distance between any two points. The simple case where one of these points is the origin will be first dealt with.



Let $OP = d$, $\sin\theta \tan F = \tan PM = \cos\theta \tan\phi$. That is, $\tan\theta \tan F = \tan\phi$. But $\cos F \tan d = \tan\theta$. The elimination of F gives $\tan^2 d = \tan^2\theta + \tan^2\phi$, an equation of the second degree in $\tan\theta$ and $\tan\phi$ and readily seen from the hypothesis to be the equation of a small circle with the origin as centre and angular radius of d. Making the supposition that R becomes infinite, we arrive at the well-known form,

$$x^2 + y^2 = r^2.$$

VIII. The more general case will now be attempted. Let P be $(\theta\,\phi)$ and P', (θ', ϕ'); $\cos d = \sin PT \sin P'T'' + \cos PT \cos P'T'' \cos(\theta - \theta') = \cos PT \cos P'T''$ $\left\{\tan PT \tan P'T'' + \cos(\theta - \theta').\right\}$



But

$$\cos\theta \tan\phi = \tan PT;$$

and

$$\cos\theta' \tan\phi' = \tan P'T'',$$

whence $\cos d = (\cos PT \cos P'T'' \cos\theta \cos\theta')(1 + \tan\theta \tan\theta' + \tan\phi \tan\phi')$.

That is

$$\frac{1}{1 + \tan^2 d} = \frac{\cos^2\theta}{1 + \tan^2 PT} \cdot \frac{\cos^2\theta'}{1 + \tan^2 P'T''}$$

$$(1 + \tan\theta \tan\theta' + \tan\phi \tan\phi').$$

But

$$\frac{(1 + \tan^2 PT)}{\cos^2\theta} = \frac{1 + \tan^2\theta + \tan^2\phi}{1}$$

It therefore follows that

$$(1 + \tan^2 d) = \frac{(1 + \tan^2\theta + \tan^2\phi)\ (1 + \tan^2\theta' + \tan^2\phi')}{(1 + \tan\theta \tan\theta' + \tan\phi \tan\phi')^2},$$

which is an equation of the second degree in $\tan\theta$, and $\tan\phi$, and as the hypothesis indicates the equation of a small circle with centre at P' and with d as angular radius.

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No. 86: THE THEORY OF THE DIRECT METHOD OF DETERMINING TRANSPORT NUMBERS, BY W. LASH MILLER

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The theory of the direct method of determining transport numbers.

By

W. Lash Miller.

(With 2 figures in text.)

The theory of the direct method of determining transport numbers.

The transport number of any component of an electrolytic solution, as defined by Hittorf, gives the number of electrochemical equivalents of that constituent transported from one electrode compartment to another during the passage of 96 540 coulombs through the solution. It may be determined either by quantitative analysis of the contents of the electrode compartments before and after the passage of a measured amount of electricity (Hittorf's or analytical method), by observation of the motion of the boundary separating two solutions (meniscus or direct method), or by thermodynamic inference from E. M. F. determinations etc. (thermodynamic method).

The theory of the 'direct' method has been developed by Kohlrausch[1]), Weber[2]), Masson[3]), Abegg[4]) and others, but among the experimental workers in this field the impression seemes to have grown up that 'directly' determined transport numbers need not necessarily agree with those obtained by the analytical method[5]). The following argument, which differs from those of Kohlrausch and others in avoiding all references to rates, mobilities, current, and other functions involving time, and which makes no assumption as to the constitution (whether complex or not) of the ions of the solutions involved, shows that transport numbers properly calculated from observations of the motion of the meniscus must be identically the same as those obtained

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[1]) Wied. Ann. **62**, 237 (1897).

[2]) Ber. d. d. chem. Ges. 936 (1897).

[3]) Zeitschr. f. physik. Chemie **29**, 501 (1899).

[4]) Zeitschr. f. physik. Chemie **40**, 737 (1902).

[5]) For instance, Zeitschr. f. physik. Chemie **44**, 575 (1903); Phil. Trans. **205 A**, 99 (1905).

by the analytical method; in fact, that the 'meniscus method' is but a modification of the method of Hittorf, in which the amounts of the various constituents of the solution transported are determined by volume measurements instead of by quantitative chemical analysis.

Two salts with common ion.

Figure 1 represents the longitudinal section of a cylindrical tube of radius r, through which the (positive) electric current flows in the direction indicated by the arrow. At the beginning of the experiment the tube is filled with solutions of AS and AZ, meeting at ab; and it is assumed that the boundary between these solutions (hereafter termed the "meniscus") although moving along the tube, remains sharp

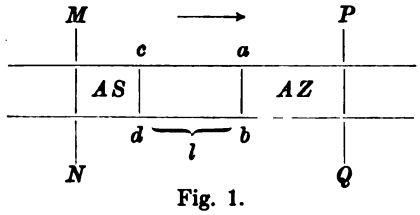

Fig. 1.

and distinct throughout the experiment. Under the influence of the current the constituent A of the solutions moves in the direction of the positive current of electricity, S and Z move in the opposite direction; so that, in Faradays sense although not necessarily in the sense of the modern theory of solutions, A, S and Z are the 'ions' present.

Let cd, at a distance l cm. from ab, represent the position of the meniscus after the passage of 96540 coulombs; $\pi l r^2$ cc of the AS solution have therefore been replaced by a solution of AZ. The remaining solution of AS, to the left of cd, retains its original composition[1]), and consequently $\pi l r^2 \Sigma$ grams of the component S (Σ representing the number of grams of S in one cc of the AS solution) must have passed the stationary section MN. This number, $\pi l r^2 \Sigma$, may be termed the "uncorrected gram transport number" of the ion S; and if the concentration be expressed in gram equivalents of S per cc, σ, then $\pi l r^2 \sigma$ gives its "uncorrected equivalent transport number". Hittorf's transport number is defined as the number of equivalents of S which during the

[1]) The concentrations and the electrical conditions are the same at any two sections through the homogeneous solution, consequently the amounts transported through the two sections must be the same, and there can be no accumulation or change of concentration between them.

passage of 96540 coulombs cross a boundary stationary with respect to the water of the solution, not, like MN, stationary with respect to the walls of the tube; hence the use of the word "uncorrected". Neglecting the correction, and writing n_s for Hittorf's transport number, and N_s for the gram transport number,

$$\pi l r^2 \Sigma = N_s \quad \pi l r^2 \sigma = n_s. \tag{1}$$

This is the fundamental expression connecting the transport number with the motion of the meniscus; it shows (1) that, subject to a correction for the expansion and contraction caused by electrolysis, the transport number as defined by Hittorf may be deduced from observations of the motion of the meniscus, no matter whether the ions of the solution be 'complex' or 'simple'; and (2) that in carrying out the experiments, the quantities to be determined are: the concentration of the solution, the cross-sectional area of the tube, and the distance moved per coulomb by the meniscus.

The concentration (Z', ζ') of the new solution of AZ formed to the right of cd by the electrolysis, is not necessarily the same as that of the solution with which the tube was originally filled (Z, ζ); nor does the meniscus separating these two AZ solutions necessarily remain fixed at ab. If however it be supposed that the tube was originally filled with a solution of AZ of the concentration Z', it is obvious that

$$\pi l r^2 Z' = N_Z' \quad \pi l r^2 \zeta' = n_Z \tag{2}$$

because the lefthand member gives the number of grams (or equivalents) of Z which during the passage of 96540 coulombs have crossed the stationary section PQ; and as the motion of the meniscus $AS|AZ$ is independent of the existence of a meniscus $AZ_{\text{conc.}}|AZ_{\text{dil.}}$, it is allowable to apply Equ. (2) in the general case, where the concentration of the new solution (Z') differs from that of the original (Z). Methods of determining the transport number based on Equ. (2) are more difficult of execution than those based on Equ. (1), because they involve an experimental determination of ζ', while σ is known.

From (1) and (2) there follows

$$\frac{N_s}{N_Z} = \frac{\Sigma}{Z'}, \quad \frac{n_s}{n_Z} = \frac{\sigma}{\zeta'} \tag{3}$$ [1]

a relation, like (1) and (2), wholly independent of special assumptions.

[1]) Kohlrausch, loc. cit. p. 238; Masson, loc. cit. p. 515.

Two solutions of different concentrations.

If in place of solutions of two salts, AS and AZ, the cylinder be supposed filled with two solutions of the same salt AZ but of different concentrations viz: Z and Z' grams (or ζ and ζ' equivalents) of the constituent Z per cc respectively, the same method of argument may be employed. To fix the ideas, let Z be greater then Z'; if then the transport number of the anion Z increase with the concentration of the solution, the meniscus will move against the current in fig. 2, and vice versa. After the passage of 96540 coulombs, n_Z equivalents

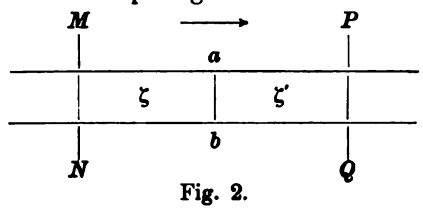

Fig. 2.

of Z have passed MN, and only n'_Z have passed PQ; so that if it be assumed that the solutions on either side of the meniscus retain their initial concentrations,

$$n_Z - n'_Z = \pi l r^2 (\zeta - \zeta')$$

$$\text{whence } l = \frac{1}{\pi r^2} \; \frac{n_Z - n'_Z}{\zeta - \zeta'}. \tag{4}$$

Absence of motion would consequently indicate that the transport number was independent of the concentration of the solution[1]).

In any attempt to realize the conditions of the argument in practice, the boundary between the two solutions of different concentrations would consist of a more or less broad diffusion band; this may be considered as consisting of a number of parallel "menisci" between pairs of solutions whose concentrations increase from ζ' to ζ in fig. 2. Assuming that n_Z increases with increase in the concentration, all of these will move against the current; and if n_Z be a linear function of the concentration, *i. e.*, if $\frac{dn_Z}{d\zeta} = \frac{n_Z - n'_Z}{\zeta - \zeta'} =$ const., all will move the same distance, and the breadth of the diffusion band will not be affected by the migration. If however $\frac{n_Z - n'_Z}{\zeta - \zeta'}$ decrease with increase in ζ, *i. e.* if $\frac{d^2 n_Z}{d\zeta^2}$ be negative, the menisci to the right in fig. 2 will overtake those to the left, thus sharpening the boundary, and vice versa[2]).

[1]) Kohlrausch, loc. cit. p. 235.
[2]) Kohlrausch, loc. cit p. 236.

Conditions of maintenance of meniscus.

Thus the method of the present paper enables one, in a simple case, to predict the effect of current on the stability of the meniscus itself. To solve the problem in general however, it is necessary to discuss the result of electrolysing a solution whose concentration (as regards one ion at least) varies along the path of the current; under these conditions the assumption made on page 437 (that the composition of the solution at any point is unaffected by the passage of the current) can no longer be made, and the simple method of treatment employed in this paper is inapplicable. Whetham's principle[1]) — that to ensure a sharp meniscus the specifically slower ion must follow the specifically faster — is of great practical utility, and Kohlrausch has deduced a number of generalizations applicable to solutions in which the mobilities of the ions involved do not vary with their concentrations (total dissociation)[2]); but the general solution can be attained only through the application of Arrhenius' theory of electrolytic dissociation, and in particular his theory of isohydric solutions[3]), to establish the necessary connection between the concentrations and the (empirical) mobilities of the components of a solution containing several salts.

Arrhenius has shown, for instance, that in an aqueous solution containing acetic acid and sodium acetate in approximately equal quantities, the dissociation of the acetic acid and consequently the participation of the hydrogen ion in the transport of an electric current is very slight; it follows from this, that a stable meniscus may be expected between acetic acid and sodium acetate solutions if the (positive) current flows from the former to the latter, *i.e.* if the hydrogen ion follows the sodium ion. Experiments by Mr. Dawson and Mr. Graham in this laboratory confirm this conclusion, and, it is hoped, may lead to a satisfactory determination of the transport number of acetic and other weak acids by the direct method.

Summary.

1. The theory of the "direct" method of determining transport numbers may be dealt with without introducing rates, mobilities, current, or other functions involving time, and without making any assumptions as to the constitution of the electrolytes.

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[1]) Theory of Solution, p. 220 (1902).

[2]) Wied. Ann. **62**, 219.

[3]) Wied. Ann. **30**, 51 (1887); Zeitschr. f. phys. Chemie **5**, 1 (1890).

2. Transport numbers properly calculated from observations of the motion of the meniscus must be identically the same as those obtained by the analytical method; for the meniscus method is but a modification of the method of Hittorf in which the amounts of the various constituents of the solution transported are determined by volume measurements instead of by quantitative chemical analysis.

3. The problem of the stability of the boundary between two electrolytes can not be solved in general without special assumptions as to the constitution of the electrolytes, such as are afforded by Arrhenius' theory of electrolytic dissociation and his theory of isohydric solutions.

The University of Toronto, September 1908.

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SOME ESTERS OF ARSENIOUS ACID. PART II. RESORCINYL ARSENITE.

BY

WILLIAM ROBERT LANG

AND

JOHN OBINS WOODHOUSE.

From the Proceedings of the Chemical Society, 1909. Vol. 25.

180. "Some esters of arsenious acid. Part II. Resorcinyl arsenite." By William Robert Lang and John Obins Woodhouse.

Continuing the experiments described in a previous communication (Lang, MacKey, and Gortner, *Trans.*, 1908, **93**, 1364), but using one of the dihydric phenols, quantities by weight of resorcinol and of arsenious oxide corresponding with the equation below were heated to the melting point of the former in a distilling flask, connected through a weighed flask with an exhaust pump. The temperature was kept constant, and the arsenic slowly dissolved in the melted resorcinol, yielding an amber-coloured fluid becoming darker as the heating progressed, the pressure being 60 mm. The water evolved in the reaction, $3C_6H_4(OH)_2 + As_2O_3 = (C_6H_4O_2)_3As_2 + 3H_2O$, collected in the trap and was weighed as a check, due precautions being taken to prevent loss. After heating for fifty-five minutes the mixture was allowed to cool, broken up, and extracted

with hot toluene, which removed from it some resorcinol. The residue was dissolved in dry ethyl alcohol, in which these esters are soluble, when an immediate precipitate of arsenious oxide was produced. Analysis of the substance obtained on evaporation in a vacuum of the alcoholic extract proved it to contain from 5 to 6 per cent. of arsenious oxide in excess of that required by the formula $(C_6H_4O_2)_3As_2$, showing that arsenious oxide dissolved in the ester formed. To prevent this, an excess of resorcinol was employed, namely, 100 grams, and 50 grams of arsenious oxide heated with it as before, the proportions of the former to the latter being, according to the equation supposed to represent the reaction, 100 to 60; in this way an amount of resorcinol corresponding with 10 grams of arsenious oxide would, of necessity, remain unacted on and be readily extracted from the ester by a specific solvent. After an hour's heating, the solidified mass was broken up and digested in a reflux condenser with dry toluene, which extracted a considerable proportion of resorcinol. This treatment was repeated until no more resorcinol could be obtained on evaporation of the solvent. The resorcinol-free mass was analysed as follows. About 1 gram was treated with water, which caused its immediate decomposition, the solution acidified with hydrochloric acid, and the arsenic precipitated as sulphide, dried on a tared filter, and weighed. The results of numerous analyses, which closely corresponded, gave:

Found, As = 31·9. $C_{18}H_{12}O_6As_2$ requires As = 31·65 per cent.

Resorcinyl arsenite closely resembles hardened gelatin in appearance, melts at 24°, and has a specific gravity of 1·9. It is soluble in methyl, ethyl, propyl, and butyl alcohols, but insoluble in ether, chloroform, benzene, or toluene. Water, however, immediately decomposes it.

The same experiments were tried with quinol, but, so far, without success.

R. CLAY AND SONS, LTD., BREAD STREET HILL, E.C. AND BUNGAY, SUFFOLK.

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No. 88: A THIRD METHYL ESTER OF PHTHALIC ACID,
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A Third Methyl Ester of Phthalic Acid.

By C. G. Allin.

[Reprinted from the Journal of The American Chemical Society,
Vol. XXXI. No. 9. September, 1909.]

A THIRD METHYL ESTER OF PHTHALIC ACID.

By C. G. Allin.

Received July 12, 1909.

These experiments were undertaken under the direction of Professor Allan with the object of finding out whether it was possible to prepare an ester of phthalic acid corresponding to the barium salt $(C_6H_4C_2O_4Ba)_4C_6H_4C_2O_3$. This barinm salt was obtained by heating the acid salt $(C_6H_4C_2O_4)_2H_2BaH_2O$ at 120–140° until constant weight was obtained.

Barium Salt and Ethyl Iodide.—(*a*) Five g. of the barium salt and 5 cc. ethyl iodide were shaken for several hours at room temperature.

(*b*) Five g. of the barium salt and 5 cc. ethyl iodide with 3 cc. ethyl alcohol were shaken for several hours at room temperature.

(*c*) Five g. of the barium salt and 5 cc. ethyl iodide were heated at 100° for two hours.

The contents of each of these tubes were then treated with water and tested for barium iodide with negative results in each case. This indicated that no ester had been formed.

Barium Salt and Methyl Sulphate.—(*d*) 0.5 g. of the barium salt and 5 cc. methyl sulphate were shaken for four hours at room temperature. When the liquid was removed, the solid part was found to contain barium sulphate, which showed that a reaction had taken place.

(*e*) Barium salt and methyl sulphate were heated in a sealed tube at 100° for four hours and then filtered. Part of the filtrate was shaken with water to decompose the methyl sulphate but all the oil disappeared, the ester being saponified by the sulphuric acid from the methyl sulphate. Another part of the filtrate, on standing, separated into two layers, one of which was found to contain much more sulphate than the other. The part containing least sulphate was washed with water, dried over sulphuric acid and saponified with potassium hydroxide solution.

0.1500 gram of the oil required, 12.17 cc. potassium hydroxide sol.
Calculated for dimethyl phthalate, 16.13 cc.
Calculated for monomethyl phthalate, 18.59 cc.

This showed that this oil was, at any rate, not the pure ester corresponding to the barium salt, as the potassium hydroxide solution required to saponify it would be intermediate between that required for the monomethyl ester and that necessary for the dimethyl ester. Other experiments showed that when the neutral barium salt or the acid salt was

heated with methyl sulphate the resulting liquid separated in each case into two layers.

(*f*) The barium salt and methyl sulphate were heated in a sealed tube for forty-five minutes. The liquid was filtered off hot and on cooling, a small quantity of white crystals separated out, which were washed free from methyl sulphate by benzene and recrystallized several times from ethyl acetate and finally gave a constant melting point of 187°. More of this product was obtained by washing the solid contents of the tube with ethyl acetate. That this substance is a compound of phthalic acid was shown by decomposing a small portion of it and obtaining the characteristic crystals of phthalic anhydride, but the melting point of monomethyl phthalate is 85° and dimethyl phthalate is a liquid.

Determination of the Methyl (Zeisel's Method).—0.2012 gram of the ester was heated with hydriodic acid in a current of carbon dioxide, the methyl iodide formed being passed into silver nitrate solution. Weight of silver nitrate formed = 0.4060 gram. Methyl found, 12.9 per cent. Calculated for $[C_6H_4(CO_2CH_3)_2]_4C_6H_4C_2O_3$, 13.0 per cent.

Determination of the Molecular Weight.—A molecular weight determination was made by finding the increase in the boiling point of acetone when the ester is dissolved in it.

Calculated for $[C_6H_4(CO_2CH_3)_2]_4C_6H_4C_2O_3$	924
Calculated for $[C_6H_4(CO_2CH_3)_2]_4C_6H_4C_2O_3/4$	231
Found	233

The substance was recovered from the acetone with unchanged melting point.

The most reasonable explanation of the molecular weight in acetone is that the ester is mostly dissociated into dimethyl phthalate and phthalic anhydride and recrystallizes from the acetone as the original ester. In that case, the easiest method of making the ester would be to dissolve these substances in acetone in the proper proportions and allow to crystallize.

0.21 g. of phthalic anhydride and 1.10 g. of dimethyl phthalate were dissolved in acetone and allowed to stand for half an hour. When the acetone was evaporated, the same weight of phthalic anhydride was found as was used and no crystals of the new ester. This shows conclusively that the ester is not dissociated into phthalic anhydride and dimethyl phthalate in acetone solution.

It is possible that the barium salt used might contain some of the salt $(C_6H_4C_2O_4)_5H_2Ba_4$ although there is no evidence that this is an intermediate stage in the preparation of the barium salt used in these experiments. If the ester were formed from this salt, it might be considered that the ester was a double compound of dimethyl phthalate and phthalic acid or of dimethyl phthalate and monomethyl phthalate, but attempts to obtain the ester by dissolving these substances in acetone and crystallizing gave the original materials only and none of the new

ester. If the ester were derived as suggested, its formula would be

$$[C_6H_4(CO_2CH_3)_2]_4C_6H_4(CO_2H_2) \div 4 = C_6H_4(CO_2CH_3)_2[C_6H_4(CO_2H_2)]_{\frac{1}{4}}$$

but with the data we have at present, the only formula which can be used is

$$C_6H_4(CO_2CH_3)_2.(C_6H_4\langle{}^{CO}_{CO}\rangle O)_{\frac{1}{4}}.$$

It is hoped that measurement of the rate of saponification of dimethyl phthalate or of the rate of esterification of phthalic acid or of phthalic anhydride by methyl alcohol will show whether this new ester is an intermediate stage in one or more of these reactions.

Only about 0.6 g. of this ester has been prepared as the yield is very poor. This is probably due to the barium salt becoming protected by a layer o barium sulphate and it is hoped that some method of shaking the tube may increase the yield. Further investigation of this very interesting ester is in progress.

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[Reprinted from the Journal of The American Chemical Society,
Vol. XXXII, No. 1, January, 1910.]

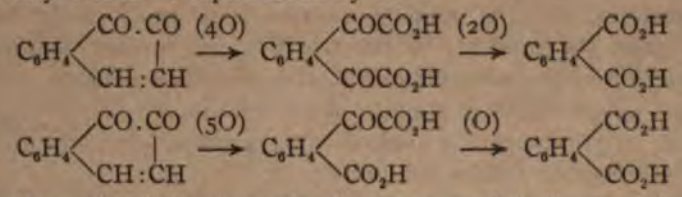
NOTE ON THE OXIDATION OF β-NAPHTHOQUINONE.

By C. H. Robinson.

Received November 1, 1909.

In a series of experiments on the oxidation of naphthalene and various naphthalene derivatives, Daly[1] found some indications that in the oxidation of β-naphthoquinone by potassium permanganate in alkaline solution the reaction ceased before the amount of permanganate had been reduced which would correspond to the oxidation of the naphthoquinone to phthalonic acid and he mentions the possibility of the diketo acid, $C_6H_4(COCO_2H)_2$, being formed in the solution. Under the direction of Professor Allan, the author investigated this reaction in the hope of preparing the diketo acid in this way.

If the oxidation in alkaline solution were to the diketo acid and then in acid solution to phthalic acid the two stages of the reaction might be represented by A, but if the oxidation in alkaline solution were to phthalonic acid they would be represented by B.



So that the ratio of the amounts of oxygen used in the two stages of the reaction would be two according to A or five according to B.

The β-naphthoquinone was prepared by the method of Lagodzinski and Hardine[2] and purified by the method given by Boswell.[3] It is slightly soluble in decinormal sodium bicarbonate solution (0.54 g. per liter) and not more soluble in a normal solution.

To find the ratio between the amount of permanganate required to oxidize the naphthoquinone in alkaline solution and the permanganate required to complete the oxidation in acid solution to phthalic acid, 110 cc. of a saturated solution of the quinone in decinormal sodium bicarbonate was added to 50 cc. decinormal permanganate solution and left at laboratory temperature for twenty-four hours. In 50 cc. of this solution the residual permanganate was determined by adding a solution of 0.4 g. potassium iodide and 2 g. sulphuric acid in 100 cc. water and titrating the iodine set free. To another 50 cc. of the solution two

[1] *J. Phys. Chem.*, 11, 105.
[2] *Ber.*, 27, 3075.
[3] This Journal, 29, 230.

per cent. sulphuric acid and a few drops of manganese sulphate solution were added, and after two minutes, by which time the oxidation to phthalic acid was complete, the solution of potassium iodide and sulphuric acid was added and the iodine determined. Since the oxidizing power of the permanganate is 1.66 times greater in acid solution than in alkaline solution, the permanganate used in oxidizing the solution to phthalic acid was multiplied by 1.66 so that the amounts of permanganate would be in proportion to their oxidizing value.

	I.	II.
$\frac{\text{Permanganate reduced in alkaline solution}}{\text{Permanganate reduced in acid solution}}$	4.65	4.75

This shows conclusively that the oxidation is as represented above in B and that the reaction in alkaline solution proceeds to phthalonic acid, but it is still possible that there is a rapid oxidation to the diketo acid and then a slower oxidation to phthalonic acid.

Some experiments were made to determine the constituents of the solution at various stages of the oxidation by adding small amounts of permanganate to the quinone solution, allowing the reaction to proceed till all the permanganate was reduced, acidifying the solution and ethering out. As the residual quinone is so much more insoluble in water than the products of the reaction, the residue obtained by the evaporation of the ether contained little else than quinone.

A = initial weight of quinone in the solution.
B = cc. permanganate used to 50 cc. quinone solution.
C = weight of residue from ether.
D = weight of quinone which would be left if oxidation were direct to phthalonic acid.
E = weight of quinone which would be left if oxidation were to diketo acid.

A. Gram.	B. cc.	C. Gram.	D. Gram.	E. Gram.
0.0226	1	0.0209	0.0210	0.0206
0.0226	6	0.0126	0.0131	0.0108
0.0226	8	0.0110	0.0100	0.0068
0.0226	10	0.0087	0.0069	0.0023

The results given in this table are not very good because the method was inaccurate but they confirm the conclusion arrived at from the previous experiments that there is no intermediate stage in the oxidation of β-naphthoquinone to phthalonic acid in alkaline solution. A series of experiments, in which the rate of oxidation of the quinone in alkaline solution was determined, also gave no indication of the existence of an intermediate product.

Further experiments to prepare the diketo acid by the saponification of phthalyl cyanide are now being carried out.

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ETHYL TANNATE.

By R. J. Manning.

Received June, 1910.

Of the naturally occurring tannins gallotannic acid, obtained from gallnuts and many other sources, is the most important and best known. Strecker[1] claims that gallotannic acid is a glucoside of gallic acid as it yielded gallic acid and glucose on hydrolysis. Schiff[2] synthesized di-

[1] *Ann.*, 90, 340.
[2] *Ibid.*, 170, 49.

gallic acid from gallic acid by means of phosphorus oxychloride and claims that digallic acid and gallotannic acid are isomers. If this were so, gallotannic acid would have a formula $C_{14}H_{10}O_9$ and on hydrolysis would yield no glucose. On account of the difficulty in purifying the tannin, determinations of its composition vary with different experimenters. I have prepared a crystalline ester and through it have obtained satisfactory analyses giving the composition of gallotannic acid and considerable information about it.

Description of the Gallotannic Acid Used.

The material used in these experiments was obtained through Lyman Bros., Toronto, from the German firm of Schering, and came in the form of light whitish brown flakes; extracted with ether in a Soxhlet, all dissolved, leaving a slight brown stain on the shell, soluble in boiling water. It was purified by the method described by Walden:[1] 100 grams of the commercial tannin were dissolved in 250 grams of amyl alcohol (which must contain a little water) and 350 grams of ether were added; no precipitate appeared. The tannin was then thrown down by gasoline, filtered and dried in a vacuum desiccator over sulphuric acid. So purified, it formed a whitish, rather heavy powder.

The crude sample of tannin contained a trace of gallic acid detected by the potassium cyanide method;[2] the purified product was free from this if excess of gasoline were not added during purification, and in every respect, except solubility, behaved like gallotannic acid as described in Allen's "Commercial Organic Analysis."[3]

Hydrolysis.—A dilute aqueous solution, after boiling for half an hour, reduced Fehling's solution (glucose) and gave a distinct red with potassium cyanide (Young's test for gallic acid); the same result is obtained by boiling for a moment with dilute hydrochloric acid. After long boiling with calcium carbonate while a current of air passed through the solution, the blue coloration changing to red with acids (which is characteristic of gallic acid) was observed.

Behavior with Reagents.—*Arsenic acid* in 5 per cent. alcoholic solution, warmed with its own volume of a 10 per cent. solution of the tannin, solidified to an insoluble jelly, which on standing in the air dried up to a garnet colored mass. *Ammonium molybdate* and *potassium ferricyanide*, reddish colorations; *lime water*, white precipitate quickly turning blue; *ferric chloride*, blue-black precipitate, soluble in much water; *lead acetate or nitrate*, white precipitate in not too dilute solutions; *silver nitrate*, silver mirror on warming; *copper sulphate*, greenish blue gelatinous precipitate turning black on warming; *potassium permanganate* in alkaline

[1] *Ber.*, 31, 3167 (1898).
[2] S. Young, *Chem. News*, 48, 31.
[3] Vol. III, Part I, pages 35–38 (1900).

solution, red-brown precipitate, dissolving on warming to a yellow-brown solution which becomes wine-red in the air; dilute *sulphuric acid* and dilute *hydrochloric acid*, and *concentrated salt* solutions form precipitates in moderately concentrated solutions of the tannin, which dissolve again on adding water.

Solubility.—My preparation was soluble in water, glycerol, ethyl acetate, and acetone; slightly soluble in anhydrous amyl alcohol, ether or ethyl alcohol; very slightly soluble in carbon disulphide, benzene and gasoline. It is quite insoluble in chloroform (the gallotannic acid and chloroform were shaken together and filtered, but the filtrate gave no coloration whatever with ferric chloride).

Allen[1] says that gallotannic acid is soluble in six parts of cold water; my preparation was much more soluble. In an experiment in which the tannin and water were shaken together in a thermostat at 0°, many successive portions of tannin kept dissolving until the liquid was a thick sirup, and further addition of the solid balled together and dissolved with extreme slowness. In the end the perfectly clear brownish sirup contained less than one and a half grams of water to one of tannin. At 32° the saturated sirup was still thicker, and contained more than two grams of tannin to one of water.

The solubility of tannin in ether, amyl alcohol, and ethyl acetate, is greatly increased by the addition of a trace of water, as shown by the following data:

One gram of	Dissolved at 15°
Ethyl acetate (Kahlbaum)	0.2 g. tannin
" " with 5 per cent. water by volume	2.5 " "
Amyl alcohol normal (Kahlbaum)	0.1 " "
" " with 5 per cent. water by volume	0.84 " "

The solubility of mannose, glucose, galactose, cane sugar and of the glucosides, saponin, salicin, and amygdalin in amyl alcohol, acetone, and in ethyl acetate, is also much increased by the addition of a trace of water but not so markedly as in the case of tannin. The solubility of the alkaloids, strychnine and brucine, in ethyl acetate and in acetone, on the other hand, is not markedly increased by the addition of water.

In these solubility determinations the method of analysis for gallotannic acid was that described by F. Jean,[2] involving titration with iodine in alkaline solution.

Analysis of Gallotannic Acid.

To insure perfect dryness the tannin was heated in a hot air bath at 110° for two hours.

(*a*) The elementary analysis gave the following results:

[1] *Commercial Organic Analysis*, 3rd Ed., Vol. III, Part I, page 34.

[2] *Chem. Centr.*, 1900, I, 1107.

Calculated for $C_{41}H_{22}O_{26}$:	C, 52.35; H, 3.40.
Found:	C, 52.4, 52.25; H, 3.45, 3.49.

(*b*) To estimate the glucose in tannin, the following procedure was adopted: 0.2 to 0.5 gram of the tannin was boiled with 200 cc. water and 25 cc. of 10 per cent. hydrochloric acid for an hour. As gallic acid has a marked reducing action on Fehling's solution, it was removed by extraction with ether, and as glucose itself is somewhat soluble in water-saturated ether, the extraction was carried on quantitatively and a correction applied as follows:

From 0.1 to 0.25 gram glucose was mixed with 0.5 to 1.2 grams ethyl gallate and the mixture dissolved in 200 cc. water and 25 cc. of 10 per cent. hydrochloric acid. After boiling the solution for an hour, it was made up to 100 cc. and extracted six times by shaking up for ten minutes each time with 50 cc. of ether. After the sixth extraction, all the gallic acid formed by the hydrolysis of the ether except a slight trace had been removed. The following percentages of the original glucose were found by analysis in the aqueous layer:

Glucose	78.9	79.0	78.8	78.6 per cent.

Hence the boiled solution of tannin was extracted six times with ether, the free hydrochloric acid neutralized with sodium carbonate, the glucose estimated and the results multiplied by 100/79.

The analysis gave glucose: 19.0, 18.79 per cent. Calculated on the assumption that one formula weight of the tannin on hydrolysis gives one formula weight of glucose: 19.1 per cent.

(*c*) Formula weight determinations from the boiling point of solutions:

Water as solvent	813	843	922	1025	1500
Acetone as solvent	1672	2023	1500	1450	....
Water as solvent (from freezing point)	1957	1942	1769	1956	1972

Calculated for $C_{41}H_{22}O_{26}$: 940

Preparation of the Ethyl Ester of Gallotannic Acid.

50 grams of the tannin were dissolved in 250 cc. of Kahlbaum's 99.8 per cent. ethyl alcohol. After introducing the light brown solution into a 500 cc. flat-bottomed flask, hydrogen chloride gas, dried by passing through 18 inches of pumice stone moistened with sulphuric acid, was bubbled through for at least two and a half hours. During the operation the temperature of the liquid rose to about 60°. By cooling the solution during the passage of the gas through it, the yield was diminished, while applying heat to the flask did not noticeably increase the amount of the ester formed.

The dark brown sirup left after the passage of the hydrogen chloride gas was evaporated in a large porcelain evaporating dish until quite thick, and Kahlbaum's lime-free barium carbonate added in excess. The sticky mass was extracted three times with anhydrous ether, the result-

ing greenish brown ethereal liquid allowed to evaporate, and the residue heated for some hours in a water bath. A dark greenish brown powder remained.

The crude ethyl tannate so obtained was purified by extraction with chloroform in a Soxhlet for two days. This leaves behind the coloring matter and unaltered tannin but dissolves any ethyl ga late as well as the ethyl tannate; hence the necessity of using tannin as free as possible from gallic acid. During the extraction the ethyl tannate separated out of the chloroform in the form of pale yellow spherical nodules of about 2 mm. in diameter. The yield was about 40 per cent. of the tannin used.

In the hope of obtaining a better yield, 50 cc. of benzene[1] were added to the dark brown solution through which the hydrochloric acid gas had been passed, the whole well shaken and the benzene distilled off. After three successive treatments with benzene, the liquid left in the distilling flask was evaporated and treated with barium carbonate and ether as before. This method gave no better yield and was therefore not used again.

Description of the Ethyl Tannate.

On splitting open these nodules, they were seen to consist of a mass of light yellow shining crystals radiating from a common center. Their melting point was 157° (ethyl gallate melts at 141°).[2] They were readily soluble in ether, alcohol and water; slightly soluble in chloroform; insoluble in gasoline and in carbon bisulphide. Their aqueous solution resembled a solution of tannin in its reactions with ammonium molybdate, lead nitrate or acetate, silver nitrate, copper sulphate, and potassium permanganate. With potassium cyanide the aqueous solution of ethyl tannate always gave a slight red color indicating the presence of traces of gallic acid or its ester.

Analysis of the Nodules.

(*a*) *Elementary Analysis.*—The substance was mixed with a little carefully dried red lead and ignited in a porcelain boat.

The analysis gave:	C, 52.3	52.4	52.35:	H, 5.25	5.11	5.25
Calculated for $C_{51}H_{52}O_{32}$:	52.30			5.30		

(*b*) *Loss of Water on Heating.*—To estimate the percentage of water, the nodules were heated in an air bath to 125–135° for two hours. On first heating they became rather sticky, but did not melt completely, and on continued heating became drier again but showed a tendency to turn brown and to sublime. Hence care had to be taken not to allow the temperature to rise over 135°.

The analysis gave: 7.6, 7.5, 7.8 water; calculated for $C_{51}H_{52}O_{26}\cdot 5H_2O$: 7.69 per cent.

[1] *J. Chem. Soc.*, 88, 852 (1905).

[2] Etti, *Ber.*, 11, 1882.

(*c*) *Ethoxyl Determination.*—The method used was that of Zeisel as described in Meyer and Tingle's "Estimation of Organic Radicles," pp. 34–48. In some of my determinations the precipitate of silver iodide was brownish instead of yellow. The results with these colored precipitates varied widely, being too large, and hence were rejected. It was found afterward, however, that if the brown silver iodide precipitates in these high results were boiled for five minutes with 100 cc. of 15 per cent. nitric acid, filtered and weighed, the precipitates regained their normal color and the new results agreed with those not rejected. This treatment with nitric acid does not perceptibly affect the pure silver iodide.

OC_2H_5 found: 19.24, 19.32, 19.39, 19.55, 19.55 per cent.; calculated for $C_{41}H_{37}O_{21}(OC_2H_5)_5.5H_2O$[1]: 19.23 per cent.

(*d*) *Hydrolysis of the Ester and Estimation of the Glucose.*—2 grams of the ester were boiled with 100 cc. water for two hours with a return condenser and then 25 cc. distilled off. This distillate gave no trace of alcohol when tested by the iodoform method.[1] If, however, previous to the distillation, 10 cc. of dilute hydrochloric acid or of dilute caustic potash were added to the distilling flask, the distillate then gave, especially in the latter case, a distinct deposit of iodoform.

The freshly prepared solution of ethyl tannate reduced Fehling's solution slightly; but the solution which had been boiled with acid or with caustic potash reduced Fehling's solution readily and gave a marked potassium cyanide test for gallic acid. The products of the hydrolysis are therefore ethyl alcohol, glucose, and gallic acid.

The glucose was estimated by the same method as was used for the estimation of glucose in the gallotannic acid and the same correction was applied.

The analysis gave: 15.37, 15.42, 15.51, 15.13 per cent. glucose. Calculated on the assumption that one formula weight ($C_{51}H_{62}O_{31}$) of the ester on hydrolysis gives one formula weight of glucose: 15.38 per cent.

(*e*) *Estimation of the Gallic Acid.*—0.2 to 0.3 gram of the ethyl tannate was hydrolyzed by boiling with dilute hydrochloric acid as in the estimation of the glucose. The boiled solution was then diluted to 250 cc. and the gallic acid estimated by the iodine titration method of Jean.[2]

Gallic acid found: 72.56, 72.66, 72.8. Calculated on the assumption that one formula weight ($C_{51}H_{62}O_{31}$) of the ester on hydrolysis gives five formula weights of gallic acid: 72.64 per cent.

(*f*) *Formula-weight Determinations from Boiling Point of Solutions.*—

Acetone as solvent: 255, 280, 257.
Ethyl acetate as solvent: 362, 275, 300.
Chloroform as solvent: 1335, 1000, 1200, 1467.
Water as solvent (from freezing point): 301, 309.
Calculated for $C_{51}H_{62}O_{31}$: 1170

[1] *Z. anal. Chem.*, 9, 492.
[2] *Chem. Centr.*, 1900, I, 1107.

Comparing these results, it is seen that those given by the chloroform solution are several times greater than those given by the other solutions. The lower numbers might be explained by assuming that in all the solvents but chloroform there is a dissociation into anhydrous ester and water. To test this, 0.5 to 1.0 gram of the ester was dissolved in 50 cc. acetone and the solution dehydrated carefully by introducing 10 grams anhydrous calcium chloride. After filtering and washing the calcium chloride carefully with acetone, the filtrate was diluted up to 100 cc. and its boiling point determined, giving the following results:

Formula weight found: 950, 1050. Calculated for $C_{51}H_{52}O_{26}$: 1080.

Moreover, on evaporating this solution to dryness, an amorphous, dark brown, sticky mass was left, instead of the crystalline substance before obtained.

A Higher Hydrate of the Ester of Gallotannic Acid.

On the evaporation of solutions of ethyl tannate in ether, chloroform, alcohol, acetone, and ethyl acetate, only minute crystals were obtained. To get large crystals, a cold (15°) saturated aqueous solution of ethyl tannate, obtained without heat, was allowed to evaporate in a round-bottomed evaporating dish by being placed in the sunlight. Even at that temperature a partial decomposition of the ester into ethyl gallate and glucose took place. The ethyl gallate, being less soluble, crystallized out first as a top ring of pale yellow, steep rhombic crystals around the sides of the evaporating dish. At the bottom of the vessel, on almost complete evaporation, were found large, light brown crystals, many between one and two centimeters in length, with a sticky fluid containing the glucose.

An aqueous solution of these crystals behaved like a solution of the lower hydrate of ethyl tannate. They melted at 132°[1] and effloresced readily over sulphuric acid and slowly in the air. They lost their water of crystallization on being heated at 125–135° like the lower hydrate.

Analysis gave: 20.5, 20.7, 21.0 per cent. water. Calculated for $C_{51}H_{52}O_{26}.15H_2O$: 20 per cent.

Synthesis of Ethyl Tannate from Ethyl Gallate and Glucose.

20 grams ethyl gallate prepared according to Schiff's method[2] were ground up with 5–6 grams glucose and mixed to a thin paste with phosphorus oxychloride. After heating this paste in a water bath for two hours, during which time great quantities of hydrochloric acid were given off, a dark sticky mass remained. This was further dried by heating at 120° for a couple of hours, extracted with anhydrous ether, the ether solution evaporated, and the residue again extracted with chloroform in a Soxhlet for twenty-four hours. At the end of that period a light

[1] Hydrated ethyl gallate melts at 90°.

[2] Schiff, *Ann. Chem.* **163**, 215; **170**, 72.

colored mass had settled out of the chloroform. By the fractional crystallization of its aqueous solution as previously described, the higher hydrate of the ethyl ester of gallotannic acid was obtained. This gave all the reagent tests for tannin, for glucose, and ethoxyl groups. It melted at 132°. The maximum yield I obtained was only about 5% of the theoretical.

Summary.

1. Two crystalline derivatives of tannin have been obtained. They are ethyl esters of gallotannic acid differing in the amount of water of crystallization. The previous analyses of gallotannic acid varied because crystalline derivatives were not known and therefore pure material was very difficult to obtain.

2. These esters were synthesized from alcohol and gallotannic acid and one of them was also synthesized from ethyl gallate and glucose.

3. Various analyses show that the formulas for these esters are $C_{41}H_{27}O_{21}(OC_2H_5)_5 \cdot 5H_2O$ and $C_{41}H_{27}O_{21}(OC_2H_5)_5 \cdot 15H_2O$, and that they are glucosides of gallic acid in which one formula weight of glucose and five formula weights of gallic acid are represented in one formula weight of the ester. This gives the formula $C_{41}H_{32}O_{26}$ for gallotannic acid.

4. Dissociation of the hydrated ester into water and anhydrous ester would account for the low formula-weight determinations in acetone, etc.

This work was done under the direction of Professor W. Lash Miller.

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EXPERIMENTAL DETERMINATION OF BINODAL CURVES, PLAIT POINTS, AND TIE LINES, IN FIFTY SYSTEMS, EACH CONSISTING OF WATER AND TWO ORGANIC LIQUIDS

BY WALTER D. BONNER

Comparatively little is known of the compositions of the two coexistent liquid phases which are often formed when three liquids are mixed together. The earliest determinations seem to have been made by Tuchschmidt and Follenius in 1871, but the only considerable experimental research on the subject is that published by W. D. Bancroft in 1895. Now that the graphic methods of the Phase Rule have been applied to problems of this sort, more particularly by van Rijn van Alkemade, Schreinemakers, and Roozeboom, it seemed desirable to add to the stock of experimental data, and accordingly the present investigation was undertaken.

When alcohol, for example, is gradually added to a mixture of ether and water, at some constant temperature, the compositions and quantities of the two layers of liquid gradually change, and finally a homogenous solution is obtained. The points of the "Binodal Curve" give the quantity of alcohol which must be added to any given quantities of ether and water in order to bring about homogeneity, and the extremities of the "tie lines" give the compositions of the various pairs of liquids which may exist in equilibrium. When the two layers are practically of the same composition, the tie line is reduced to a point, the "plait point," on the binodal curve.

The experimental researches hitherto published have dealt mainly with the data for the binodal curve; the positions of tie lines, that is the compositions of the various pairs of coexistent liquids, have been determined in but few cases.[1]

[1] By Waddell, Schreinemakers, Roozeboom, Wright. See Bibliography, p. 787. The paper by Duclaux contains data enough for the calculation of the tie lines.

As I wished to study as many different systems as was possible, and as organic liquids are in general costly, it was necessary to develop a method of working which would not necessitate the use of more than a few grams of material in each experiment. The difficulties of analysis were avoided by adopting a modification of the method of "quantitative synthesis" employed by Bancroft,[1] and the positions of the tie lines and plait points were determined by the graphic method described by W. Lash Miller and R. H. McPherson,[2] and applied by them in a few cases.

Method of Working

My method of working may best be described by reference to a particular case. Three Ostwald-Sprengel pyknometers with long capillary discharge tubes[3] were filled with ether, water, and alcohol, respectively, and from these 0.354 gram ether and 0.501 gram water were weighed into a cylindrical glass tube about 12 cm long and 1 cm in diameter, to the upper part of which a tube of larger bore (1.5 cm diameter and 3 cm long) had been sealed for convenience of corking. This tube was at once corked and immersed in a well stirred mixture of ice and water contained in a covered rectangular glass "aquarium" (such as is often used for gold fish) the sides of which were jacketed with felt except for a space of about 10 cm square at each end. One of these openings could be illuminated by an electric light which was extinguished except during an observation, while the other served as a window, to enable the tube to be observed through the telescope of a cathetometer. The contents of the tube were stirred by a bent wire which projected through a hole in the cork, and alcohol was gradually added from the third pyknometer (by lifting the cork and dropping in a little at a time) until a homogeneous solution was obtained. This needed 0.326 gram alcohol. The total weight of liquid in

[1] Phys. Rev., 3, 27 (1895).

[2] Jour. Phys. Chem., 12, 709 (1908).

[3] Such as are used to introduce liquids into a boiling point apparatus. See Ostwald-Luther, Physico-Chemische Messungen, 2nd edition, p. 305.

the tube was thus 1.181 grams; the cathetometer gave the height of the liquid in the tube, hence from a previous calibration, its volume; from these data its specific gravity was obtained.

The three numbers: ether 0.354, water 0.501, alcohol 0.326, fix a point on the binodal curve; but as in the graphic representation which I have adopted, the sum of the weights of ether and water is represented always by 1.00, the three numbers must each be multiplied by 1.000/0.855, giving ether 0.414, water 0.586, alcohol 0.381, as the coordinates of the point in question. In the diagram, Fig. 1, the abscissa gives the amount of ether and the ordinate the amount of alcohol; the amount of water may be obtained by subtracting the value of the abscissa from unity.[1] The other points on the binodal curve (Fig. 1) were similarly obtained.

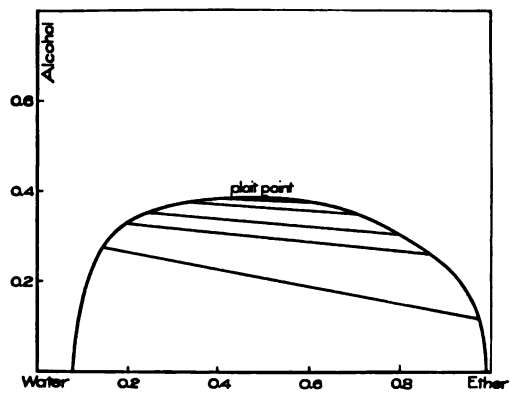

Fig. 1

The actual amount of ether used in determining the eleven points of the figure was 4.098 grams, and of alcohol 2.680 grams. About four hours work was required.

[1] This representation, while not so symmetrical as the triangular diagram, has the advantage that the ordinates are directly proportional to the weights of alcohol used in the experiments. The vertical displacement of the points of the graph due to an error of one drop of alcohol per gram of ether and water, is thus the same in every region of the diagram.

Effect of Temperature

After measuring the volume, the tube was removed from the ice bath and placed for a few minutes in a beaker of water at about 20° C. In the experiments with ether-water-alcohol, the homogeneous solutions clouded on warming and separated into two layers. In all other cases they remained clear.[1]

Determination of Plait Point and Tie Lines

As the alcohol was added in the experiment just described, the lower (aqueous) layer increased in volume, while the upper (ethereal) decreased and finally disappeared. In a subsequent experiment in which the proportions of ether and water were 0.601 and 0.399, respectively, the reverse was observed, the lower layer diminishing and ultimately disappearing. The abscissa of the plait point consequently lies between 0.414 and 0.601. To determine it more closely, 0.556 gram of ether and 0.541 gram of water were weighed out, alcohol added in successive portions and the volumes of the two layers determined by the cathetometer after each addition. The results were as follows:

TABLE I

Alcohol gram	Ether 0.556 g lower layer cc	Water 0.541 g upper layer cc	Volume ratio
0.226	0.783	0.739	0.94
0.331	0.800	0.809	1.01
0.358	0.807	0.815	1.01
0.394	0.814	0.842	1.03
0.412	0.822	0.859	1.05
0.432	Homogenous	—	—

[1] Except in the case ether-water-alcohol, mixtures to which almost enough alcohol (or other consolute liquid) has been added to make them homogenous, become so on removing from the ice bath and cloud again when replaced. Experiments numbered 35, 39, 50 were carried out at 15° C. because of the high melting point of one of the constituents; in these cases the homogenous solutions clouded on cooling, and cleared again on warming. In Meerburg's study of the binodal curves of systems containing trimethylamine, cases analogous to that of ether-water-alcohol were met with.

If it be assumed, as a *first approximation*, that the specific gravities of the two layers are the same, the volume ratio will be the ratio of their weights. If then a straight line be drawn through the point which represents the composition ether 0.556, water 0.541, alcohol 0.226 (or ether 0.507, water 0.493, alcohol 0.206) to meet the binodal curve at each side so that the length of the portion of the line to the left of the point is 0.94 times the length of the portion of the line to the right, the points at which this line meets the binodal curve will give the compositions of the lower and upper layers, respectively, and the line will be a "tie line." The abscissa of the two ends of this line are 0.100 and 0.935, respectively. To make a *second approximation*, the volume of the lower and upper layers (0.783 cc and 0.739 cc) may be multiplied by the specific gravities of the solutions (abscissa 0.100 and 0.935), *viz.:* 0.98 and 0.79 respectively, giving 0.768 gram and 0.584 gram as the weights of the two layers, and 0.760 as the weight ratio. Shifting the line to correspond, gives 0.130 and 0.990 as the abscissa of the end points. A further approximation is in general unnecessary. Each line of Table I thus serves to place a tie line; their positions were checked by three further sets[1] of experiments with different relative quantities of ether and water. As near the plait point the tie lines are roughly parallel, the position of the plait point may be obtained graphically with fair accuracy. In the present instance its coordinates are ether 0.51, alcohol 0.39, indicated by a dot on the binodal curve (Fig. 1).

Source of Error and Precautions Taken

Nearly all the chemicals used were Kahlbaum's best, mostly from bottles opened for the occasion. In a few cases, however, where the guarantee of purity was not so good, the liquid was dried and fractionated until a satisfactory preparation was obtained.

The pyknometers were weighed to four places of deci-

[1] In general only two sets of tie line determinations were made.

mals, but only three are recorded. They were always weighed immediately before and immediately after using, even where a series of measurements with the same liquids was in progress. In some cases the liquid was blown from the pyknometer, a tube 15 cm long of calcium chloride and soda-lime being used to prevent contamination by the breath; generally, however, it was found easier to add small definite amounts by squeezing a short piece of rubber tubing attached to the upper tube of the pyknometer and plugged with a bit of glass rod.

The attempt to substitute small burettes for the pyknometers was abandoned, as it was found impossible to keep the liquids in them at constant temperature.

To guard against evaporation, the tube in which the liquids were mixed was kept stoppered. In a number of cases it was weighed after the experiment and the loss thus determined directly; with volatile liquids on long standing (as in tie line determinations) this might reach as high as one percent. Table II gives the total weights and the losses in the experiments to determine the binodal curves for toluene-water-alcohol and for chloroform-water-carbinol respectively:

TABLE II

Toluene-water-alcohol		Chloroform-water-carbinol	
Added	Loss	Added	Loss
1.3594	0.0024	1.3122	0.0118
1.6416	0.0116	1.5174	0.0120
1.7512	0.0056	1.8742	0.0088
1.5764	0.0050	2.1664	0.0140
2.4756	0.0112	2.4426	0.0153
2.5806	0.0076	2.1092	0.0110
1.8362	0.0062	1.3517	0.0067
1.6854	0.0046	—	—
0.9570	0.0070	—	—

As in all the experiments the tube was at least one-third full of liquid, the composition of the liquid was not ap-

preciably affected by the formation of vapor (at zero centi grade) within the tube.

In general there was no difficulty in deciding whether one phase was present, or two; the contents of the tube forming a more or less translucent, milky emulsion until the last drop of the consolute liquid suddenly cleared it. In a few cases,[1] ether-water-alcohol, for example, no such emulsion was formed and the end point was harder to determine. If a little lampblack[2] were added, however, it collected at the boundary between the two liquids, which thus became easily visible even when the amount of one phase was very small.

In order to get an idea of the probable accuracy with which the end point could be determined in such cases, saturated solutions of ether in water and of water in ether were made by shaking together equal volumes of water and ether. Some of the lower layer was pipetted off into a tared tube, weighed, and then the least amount of the upper layer of whose presence I could be positive was determined by adding it in very small drops until plainly visible, and then weighing. The same procedure was followed in the case of the upper layer, adding a small amount of the lower, and in both cases experiments were made with and without addition of lampblack. Using about one gram of the lower layer, and adding the upper in very small drops, I found as the mean of several trials that six or eight milligrams was the least amount of which I could be quite certain. The presence of the black does not greatly lessen the amount of the upper layer needed, but it facilitates its detection very decidedly. Before adding the upper layer the black is scattered in loose flakes over the surface or climbing up the sides of the tube; but the addition of a very small drop of the upper layer causes it to form a pronounced film on the surface, and to come down from the sides. This film forms again at once if dis-

[1] Other experiments in which this occurred were Nos. 5, 11, 21, 31, 32, 33 and 34 (see Table V).

[2] Lycopodium will not go into the boundary. Indigo, carmine, and ultramarine dissolve, or seem to, in some of the liquids used.

turbed by stirring, but on the addition of a drop or two of alcohol, enough to render the system homogeneous, it is immediately dissipated, the black for the most part settling into the liquid and slowly to the bottom of the tube.

Using about the same amount (one gram) of the upper phase and adding small drops of the lower, I found that about twenty milligrams was the least amount of which I could be positive.

Another method of detecting the end point that proved useful with some substances[1] was to warm the liquid slightly until it became homogeneous and then to cool it again in the ice bath, when the second phase would separate as an emulsion, whose disappearance on addition of the consolute liquid could easily be noted.

In determining the tie lines it was usually necessary to let the mixture stand from a half hour to several hours before it separated into two layers whose volumes could be measured. In a number of cases complete separation did not occur in six or eight hours and recourse was had to a centrifuge.[2]

On addition of alcohol to mixtures of water and *o*-xylene, the densities of the upper and lower layers approach, finally become equal, and then when more alcohol is added the "upper" layer becomes the heavier, and the two change places.[3] In this case I could not obtain good separation on standing, even for twenty-four hours, or on centrifuging. Water, mesitylene and alcohol behave in an analogous manner, but separation is not so difficult.

The tubes used were calibrated by adding weighed amounts of water (of chloroform in a duplicate calibration) and determining with a cathetometer the distance from the bottom of the glass tube to the lowest and the highest points of the meniscus.

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[1] This plan was used in experiments Nos. 24, 25, 26, 27, 28, 29 and 37 (Table V).

[2] Experiments Nos. 3, 4, 26, 27, 28, 35, 37, 39, 42, 45 and 48.

[3] This occurred in experiments Nos. 4, 8, 28, 35, 39, 41, 43 and 49.

The volume of the meniscus cannot be neglected; it was calculated from the height of the meniscus by assuming[1] that the perpendicular section of the boundary liquid-air is an ellipse. From this assumption it follows that the volume of the meniscus is directly proportional to its height. With one of the tubes, for example, the volume was 0.025 cc per mm, and the height varied from about 1.8 mm to 2.5 mm, depending on the liquids used. On a total volume of one cc the "meniscus correction" thus amounts to five or six percent.

The cathetometer was a good instrument with glass scale, each division of the scale corresponding to one mm, the tenths being easily read with a vernier. With the tubes used, 0.1 mm corresponded to about 0.01 cc, or one percent on a volume of one cc. An error of one or two percent in the density might thus easily be made. Any greater accuracy, however, would be superfluous, as the densities were only used in placing the tie lines (see page 742).

As the object of the investigation was to study a large number of substances, extreme accuracy had to be sacrificed to the necessity for working with small quantities. The abscissa of points on the binodal curve are, of course, fairly accurate, probably well within one-half percent. But since a drop of alcohol, or of the other consolute liquids used in the experiments, weighs about 0.01 gram, the ordinates may be one or two percent out. From the agreement between duplicate experiments, and from the smoothness of most of the curves, I do not believe that the error in general exceeds this amount.

In placing the tie lines, much depends on the form of the curve. The nearer the "volume ratio" approaches unity, the less the error, and I have borne this in mind when planning the experiments.

The results furnish a view of a very extensive field. If it should prove necessary to examine any portion of it more

[1] Ostwald: Lehrbuch, 1, 484.

minutely, the necessary experiments can be repeated on a larger scale. The experimental data are collected in Table V, and additional experimental details are given under "Notes on Table V," p. 757.

Discussion of the Results

Examination of Table III in which the coordinates of the plait points are collected, shows obvious stoichiometric regularities: With alcohol as consolute liquid, the three esters, ethyl acetate, propionate and isobutyrate, come together, in the order given; similarly with the three alcohols, benzyl, isobutyl and isoamyl. The hydrocarbons pinene, mesitylene, *o*- and *p*-xylene, and toluene come in the order given, but *m*-xylene stands out of its place at the head of the series. Amyl, isobutyl, propyl, and ethyl bromides follow in the order named. Speaking roughly, the latter half of the table includes the liquids noticeably soluble in water, and with the exception of chloroform, only such; while the first half is taken up with hydrocarbons, brom and nitro derivatives. Except in the case of chloroform-propyl alcohol, the plait point is shifted to the right (less water) when carbinol is replaced by ethyl alcohol and the latter by propyl alcohol.

Table V. Inspection of Figs. 2, 3 and 4 shows, however, that there is no such regularity to be observed in the relative positions of the three binodal curves: in the case of brom-benzene, the highest curve is that for methyl alcohol, then ethyl alcohol, and propyl alcohol lowest; with chloroform the order is propyl, methyl, ethyl; and with carbon tetrachloride, methyl, proply, ethyl; at the extreme left of the figures, however, the order is methyl, ethyl, propyl, in every case. In the systems hexane-water-carbinol and heptane-water-carbinol the plait point is situated practically at the origin of coordinates; in other words, no matter what the proportions of carbinol, water and hexane (heptane) may be, if two layers are formed the upper layer

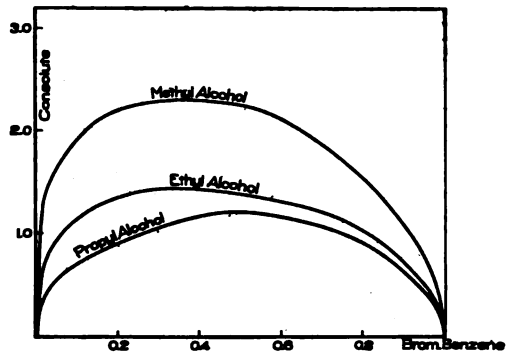

Fig. 2

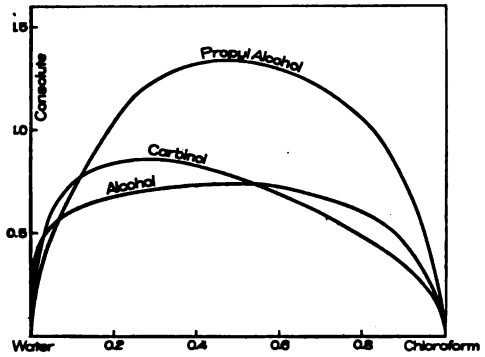

Fig. 3

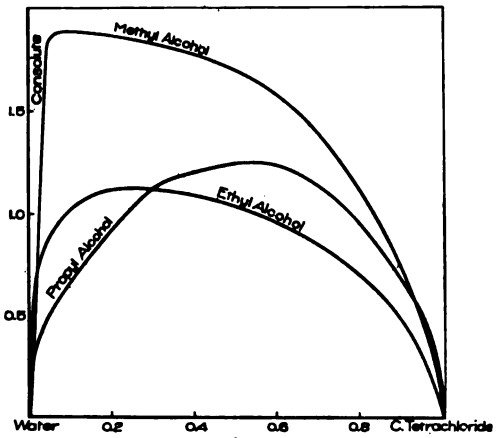

Fig. 4

will be practically pure hexane (heptane). The behavior of hexane and heptane is thus analogous to that of a solid (*e. g.* common salt) with carbinol and water: the amount

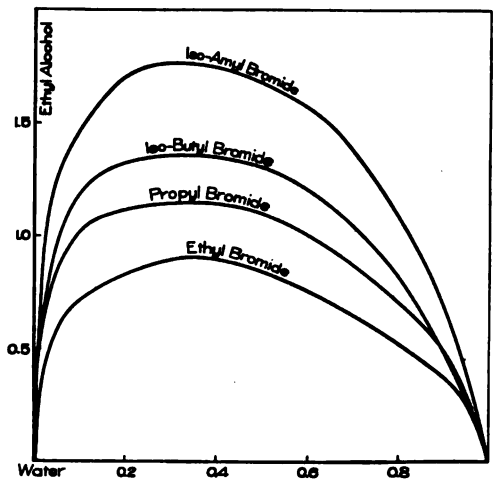

Fig. 5

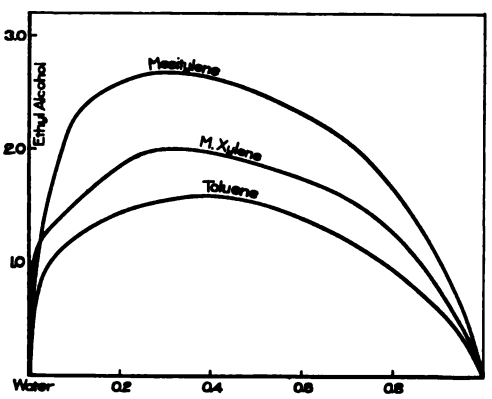

Fig. 6

dissolved varies with the proportion of water to carbinol, but neither of the latter substances is dissolved in the hydrocarbon or in the salt.

TABLE III—COORDINATES OF PLAIT POINTS

Carbinol

System number		Water	Carbinol
33	Heptane	0	0
32	Hexane	0	0
6	Carbon tetrachloride	0.015	0.215
17	Brombenzene	0.02	0.40
11	Ethyl bromide	0.05	0.33
3	Chloroform	0.27	0.57

Propyl alcohol

System number		Water	Prop. alc.
4	Chloroform	0.49–0.56	1.3
8	Carbon tetrachloride	0.75	1.06
23	Bromtoluene	0.75	0.97
19	Brombenzene	0.75–0.85	0.90
13	Ethyl bromide	0.96	0.20

Alcohol

System number		Water	Alcohol
38	*m*-Xylene	0.01	0.10
41	Pinene	0.015	0.47
22	Bromtoluene	0.02	0.33
34	Heptane	0.02	0.38
40	Mesitylene	0.03	0.58
32	Hexane	0.03	0.59
18	Brombenzene	0.04	0.32
16	Isoamyl bromide	0.04	0.36
37	*o*-Xylene	0.04	0.53
44	*p*-Nitrotoluene	0.05	0.50
15	Isobutyl bromide	0.07	0.42
7	Carbon tetrachloride	0.08	0.39
14	Propyl bromide	0.08	0.42
39	*p*-Xylene	0.08	0.57
50	Nitrobenzene	0.09	0.49
49	Phenetol	0.10	0.55
9	Ethylene chloride	0.12	0.46
12	Ethyl bromide	0.17	0.45

TABLE III—(*Continued*)

Acetone				Alcohol			
System number		Water	Acetone	System number		Water	Alcohol
20	Brombenzene	0.51	1.6	25	Benzyl acetate	0.32	0.60
5	Chloroform	0.58	1.65	28	Benz. ethyl ether	0.33	0.71
				10	Ethylidene chlor.	0.33	0.72
				43	Methyl aniline	0.34	0.72
				36	Toluene	0.35–0.50	1.4
				42	Benzaldehyde	0.43	0.61
				1	Ether	0.49	0.38
				30	Diethyl ketone	0.50	0.41
				24	Ethyl acetate	0.52	0.30
				26	Ethyl propionate	0.54	0.53
				27	Ethyl butyrate	0.54	0.67
				45	*o*-Toluidene	0.50–0.60	0.49
				2	Chloroform	0.58	0.73
				48	Benzyl alcohol	0.62	0.42
				46	Isobutyl alcohol	0.65	0.21
				47	Isoamyl alcohol	0.73	0.43

	Carbinol		Alcohol		Propyl alcohol		Acetone	
Heptane	0	0	0.02	0.38				
Hexane	0	0	0.03	0.59				
Carbon tetrachloride	0.015	0.215	0.08	0.39	0.75	1.06		
Bromtoluene	—	—	0.02	0.33	0.75	0.97		
Brombenzene	0.02	0.40	0.04	0.32	0.75–0.85	0.90	0.51	1.6
Ethyl bromide	0.05	0.33	0.17	0.45	0.96	0.20	—	—
Chloroform	0.27	0.57	0.58	0.73	0.49–0.56	1.3	0.58	1.65

Equations for the Binodal Curve

The first attempt to set up an algebraical equation for a binodal curve was made by Tuchschmidt and Follenius,[1] who found that values of x calculated from the expression

$$xy = s - \frac{c}{x + b}$$

(where y gives the number of cc of carbon bisulphide which will dissolve in 10 cc of a spirit containing x percent alcohol by weight) agreed "beinahe vollständig" with the results of their experiments.

Pfeiffer[2] "expected to be able to express the equilibrium by the formula

$$(a - x)(a - y)z = (w - z)xy$$

but the calculations were far from agreeing with the experiments."

Beginning in 1894[3] Bancroft published a series of papers on "Ternary Mixtures." He found that in a number of cases, including those investigated by himself and the alloys of Wright,[4] the curves were represented by the formula

$$xy^n = \text{const.},$$

where x and y are the amounts of the two immiscible liquids to a definite amount of consolute. In most cases, however, two equations with different constants were necessary to express the whole curve. It was thought that the corresponding logarithmic lines might cross at the plait point, but this is shown not to be the case by Waddell's experiments[5] on the system benzene-water-acetic acid and by my own measurements. Lincoln,[6] in repeating Waddell's ex-

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[1] Ueber die Löslichkeit des CS_2 in Alcohol. Ber. chem. Ges. Berlin, 4, 583 (1871).

[2] Ueber Lösungen von begrenzter Mischbarkeit. Zeit. phys. chem., 9, 444 (1892); see page 470 of his paper.

[3] Phys. Review, 3, 21 (1895), etc.

[4] See Bancroft's fourth paper, Jour. Phys. Chem., 3, 217 (1899).

[5] Jour. Phys. Chem., 2, 233 (1898).

[6] Ibid., 8, 248 (1904).

periments, found, contrary to that author, two straight lines; but the point of intersection does not correspond with the plait point given in Waddell's paper. Furthermore, in a number of the systems investigated by Bell[1] the lines plotted in logarithmic coordinates are distinctly curved, a fact that is true also in a number of my own results.

I have calculated the logarithmic coordinates for the present measurements, taking $\log \frac{w}{a}$ as ordinates and $\log \frac{1-w}{a}$ as abscissa, where w represents the weight of water and a the weight of consolute, to a total of one gram of water *plus* third liquid. The results are given under the various systems in Table V. The following list indicates the form of the corresponding graphs, the numbers referring to the System No. given in Table V.

Straight lines (between the limits of w given in the last col. of Table IV) Nos. 1, 3, 9, 11, 12, 14, 22, 25, 29, 32, 35, 36, 38, 39, 40, 41, 43, 44.

Concave upwards. Nos. 4, 8, 13, 19, 23, 28, 33, 39, 50.

Convex upwards. Nos. 2, 5, 6, 7, 10, 15, 16, 17, 18, 20, 26, 27, 28, 31, 37, 42.

Irregular. Nos. 24, 34, 45, 46, 47, 48.

In all cases where the logarithmic curve, or part of it, is straight, I have calculated, from the graphs, the two constants for the equation to the line, which for convenience has been written

$$\log \frac{w}{a} = -p \log \frac{1-w}{a} + \log \gamma \ldots\ldots\ldots\ldots (A).$$

The values of p and $\log \gamma$, calculated in this way, are given in the fifth and sixth columns in Table IV, the last column in the table showing the range of the values of w over which the line is straight.

[1] Jour. Phys. Chem., 9, 531 (1905).

TABLE IV—EQUATION CONSTANTS

System number in Table V	System: Water and	p calc'd. from $\frac{1-w}{w}$	Log. γ calc'd. from log. $\left(\frac{0.5}{a}\right)^{p+1}$	p	Log. γ	Range of w over which log. line is straight
				Calc'd. from log. graphs.		
1	Ether—alcohol	0.92	0.21	0.965	0.227	0.1–0.9
2	Chloroform—alcohol	0.89	$\bar{1}$.68	—	—	—
3	Chloroform—carbinol	0.37	$\bar{1}$.74	0.40	$\bar{1}$.72	0.2–0.9
4	Chloroform—propyl alcohol	0.89	$\bar{1}$.19	—	—	—
5	Chloroform—acetone	1.67	$\bar{2}$.57	—	—	—
6	Carbon tetrachloride—carbinol	0.11	$\bar{1}$.41	—	—	—
7	Carbon tetrachloride—alcohol	0.33	$\bar{1}$.58	—	—	—
8	Carbon tetrachloride—prop. alcohol	1.08	$\bar{1}$.18	—	—	—
9	Ethylene chloride—alcohol	0.72	$\bar{1}$.49	0.598	$\bar{1}$.522	0.1–0.9
10	Ethylidene chloride—alcohol	0.49	$\bar{1}$.68	—	—	—
11	Ethyl bromide—carbinol	0.61	$\bar{1}$.35	0.603	$\bar{1}$.354	0.1–0.9
12	Ethyl bromide—alcohol	0.51	$\bar{1}$.67	0.479	$\bar{1}$.679	0.2–0.9
13	Ethyl bromide—prop. alcohol	0.89	$\bar{1}$.34	—	—	—
14	Propyl bromide—alcohol	0.57	$\bar{1}$.46	0.553	$\bar{1}$.467	0.1–0.8
15	Isobutyl bromide—alcohol	0.49	$\bar{1}$.37	—	—	—
16	Isoamyl bromide—alcohol	0.45	$\bar{1}$.24	—	—	—
17	Brombenzene—carbinol	0.64	$\bar{2}$.93	—	—	—
18	Brombenzene—alcohol	0.47	$\bar{1}$.35	—	—	—
19	Brombenzene—prop. alcohol	0.85	$\bar{1}$.29	—	—	—
20	Brombenzene—acetone	0.82	$\bar{1}$.08	—	—	—
21						
22	Bromtoluene—alcohol	0.54	$\bar{1}$.14	0.645	$\bar{1}$.056	0.1–0.8
23	Bromtoluene—prop. alcohol	0.82	$\bar{1}$.36	—	—	—
24	Ethyl acetate—alcohol	0.64	0.28	—	—	—
25	Benzyl acetate—alcohol	0.37	$\bar{1}$.73	0.351	$\bar{1}$.734	0.2–0.9

TABLE IV—(*Continued*)

System number in Table V	System: Water and	p calc'd. from $\frac{1-w}{w}$	Log. γ calc'd. from log. $\left(\frac{0.5}{a}\right)^{p+1}$	p	Log. γ	Range of w over which log. line is straight
				Calc'd. from log. graphs.		
26	Ethyl propionate—alcohol	0.51	$\bar{1}.97$	—	—	—
27	Ethyl butyrate—alcohol	0.47	$\bar{1}.82$	—	—	—
28	Benzyl ethyl ether—alcohol	0.39	$\bar{1}.67$	—	—	—
29	Isoamyl ether—alcohol	0.43	$\bar{1}.12$	0.407	$\bar{1}.141$	0.2–0.9
30	Diethyl ketone—alcohol	—	—	—	—	—
31	Hexane—carbinol	0.92	$\bar{3}.88$	—	—	—
32	Hexane—alcohol	0.72	$\bar{2}.67$	0.666	$\bar{2}.728$	0.2–0.9
33	Heptane—carbinol	0.85	$\bar{3}.70$	—	—	—
34	Heptane—alcohol	0.79	$\bar{2}.57$	—	—	—
35	Benzene—alcohol	0.59	$\bar{1}.40$	0.540	$\bar{1}.439$	0.1–0.9
36	Toluene—alcohol	0.61	$\bar{1}.22$	0.566	$\bar{1}.258$	0.2–0.9
37	*o*-Xylene—alcohol	0.59	$\bar{1}.09$	—	—	—
38	*m*-Xylene—alcohol	0.47	$\bar{1}.15$	0.60	$\bar{1}.060$	0.1–0.9
39	*p*-Xylene—alcohol	0.57	$\bar{1}.17$	0.552	$\bar{1}.118$	0.3–0.9
40	Mesitylene—alcohol	0.43	$\bar{2}.99$	0.549	$\bar{2}.911$	0.1–0.9
41	Pinene—alcohol	0.69	$\bar{2}.66$	0.69	$\bar{2}.650$	0.1–0.9
42	Benzaldehyde—alcohol	0.43	$\bar{1}.85$	—	—	—
43	Methyl aniline—alcohol	0.45	$\bar{1}.67$	0.503	$\bar{1}.647$	0.1–0.9
44	*p*-Nitrotoluene—alcohol	0.67	$\bar{1}.06$	0.749	$\bar{1}.031$	0.2–0.9
45	*o*-Toluidin—alcohol	0.54	0.03	—	—	—
46	Isobutyl alcohol—alcohol	0.54	0.61	—	—	—
47	Isoamyl alcohol—alcohol	0.67	0.08	—	—	—
48	Benzyl alcohol—alcohol	0.64	0.16	—	—	—
49	Phenetol—alcohol	0.61	$\bar{1}.23$	—	—	—
50	Nitrobenzene—alcohol	0.72	$\bar{1}.28$	—	—	—

The following considerations will give a clearer idea of the signification of these constants in the corresponding binodal curves.

From equation (A)

$$a^{p+1} = \frac{w}{r}(1-w)^{p} \quad \ldots\ldots\ldots\ldots\ldots (B).$$

For the condition $da/dw = 0$, *i. e.*, for maximum a,

$$p = \frac{1-w}{w}$$

p, therefore, gives the ratio of the weight of immiscible liquid to water at the maximum point in the binodal curve.

For $w = 0.5$, *i. e.*, for the mixture of 0.5 gram water to 0.5 gram immiscible liquid, equation (B) becomes

$$a^{p+1} = \frac{(0.5)^{p+1}}{r}$$

or

$$r = \left(\frac{0.5}{a}\right)^{p+1} \quad \ldots\ldots\ldots\ldots\ldots (C)$$

where a is the amount of consolute necessary to make a half and half mixture of water and second immiscible liquid homogeneous.

The constants have been calculated in this way for all the experiments (including those for which the logarithmic curve is not straight) and are given in the third and fourth columns of Table IV. The logarithmic lines plotted by the use of these constants will correspond only approximately with the experiments, but will necessarily pass through the right point for $w = 0.5$. Even in the cases where the logarithmic graphs are straight the slope given by the interpolation formula may be slightly inaccurate owing to the difficulty of determining exactly the maximum point of the binodal curve.

Writing equation C in the form

$$\frac{\log r}{p+1} = \log(0.5) - \log a,$$

it will be noted that the left-hand term of the equation increases with decrease of a and *vice versa*. Since $\log \gamma$ varies in the different systems over a much wider range than $p + 1$, which with two exceptions lies between 1.3 and 2, $\log \gamma$ itself may be taken as a rough indication of the variation of a. Since, as was shown above, a is the amount of consolute required to make equal quantities of the two immiscibles homogeneous it might be expected that $\log \gamma$ would be small for the very insoluble pairs and *vice versa*. That this is approximately true is shown by the following list in which the systems are arranged in ascending order of $\log \gamma$ (the numbers refer to the System Nos. in Table IV):

Ascending order of $\log \gamma$: Nos. 33, 31, 34, 5, 41, 32, 17, 40, 44, 20, 37, 29, 22, 38, 39, 8, 4, 49, 36, 16, 50, 19, 13, 11, 18, 23, 15, 35, 6, 14, 9, 7, 28, 12, 43, 2, 10, 25, 3, 27, 42, 26, 45, 47, 48, 1, 24, 46.

It will be noted that the first part of the list contains heptane, hexane, pinene, brombenzene, mesitylene, etc., while in the latter part there are isobutyl alcohol, ethyl acetate, ether, etc.

Notes on Table V

Table V contains the data from the various measurements made. In all the experiments water was one of the non-miscible pair and so has been omitted in the headings, the names of the second non-miscible liquid and of the consolute liquid being used to designate the system. The columns headed "water" give the weight of water; the weight of the second non-miscible liquid in the system, and hence the abscissa in the graphs, may be found by subtracting the amount of water from unity. The second column (headed carbinol, alcohol, propyl alcohol or acetone) gives the weight of the consolute liquid necessary to make a homogeneous solution, *i. e.*, the ordinate in the graphs. These two numbers fix a point on the binodal curve. The figures in the "density" column are the densities of the homogeneous systems as determined by the cathetometer. For the convenience of any who may desire to use these results, interpo-

lations of the even decimals have been made and inserted in the table; these interpolations which have been made from the plotted curves are given to two decimal places only, and are marked by an asterisk. The plait points are inserted in the tables in their proper places, and are indicated by the letters P. P. The two small columns headed "water-water," which appear at the bottom of most of the tables give the abscissa of the two ends of the tie lines. The lower, denser, phase is always given in the first column. The tables of logarithmic coordinates are referred to under "Equations for binodal curve," p. 752.

The temperature of the experiments was zero centigrade except where otherwise stated.

(4) Near the plait point separation was very slow; no even dividing line between the phases could be obtained.

Plait point between water 0.49 and 0.56:

(5) These mixtures do not become cloudy to any great extent. Near the plait point the two phases are so nearly the same in appearance that without the lamp black it was very difficult to see the dividing line.

(7) Kahlbaum's preparation, freshly distilled, b. p. 78°.

(9) The ethylene chloride was dried and redistilled, b. p. 83°–84°.

(11) The ethyl bromide was prepared in the laboratory. It was dried and fractionated, b. p. 38°–39°.

(13) The plait point seems to lie between the points water 0.950 and water 0.969, but though repeated attempts were made no tie lines were obtained.

(14) The first three tie lines are a first approximation only, but the radiation from the origin indicates that the bottom layer during the first part of the experiment was practically pure propyl bromide.

(17) The brombenzene was prepared by students in the organic laboratory. A fraction of 100 cc boiling at 154° was used for these measurements.

(19) Separated very slowly near the plait point. Did

not separate on standing twenty-four hours. Centrifuging was of no help.

Plait point between water 0.75 and 0.85:

(21) It was impossible to determine the end point accurately because the bromtoluene phase settles to the bottom as oily drops in a perfectly clear liquid, and the end could be determined only by the disappearance of the oily drops. The bromtoluene was freshly distilled, b. p. 182°–183°.

(24) At 0°, 10 grams ethyl acetate dissolve 0.301 gram of water. Ten grams of water at 0° dissolve 1.086 grams of ethyl acetate.

(28) Benzyl ethyl ether forms at first the upper layer. After the addition of a little alcohol it forms the bottom layer.

(29) The first two tie lines given are first approximation only.

(30) It was not found possible to carry this curve beyond the point water 0.70. From this point on, after the addition of a small amount of alcohol the mixture no longer separates into two layers but remains turbid and a great excess of alcohol does not remove this turbidity.

Plait point only near water 0.50:

(31) The hexane and heptane used were Kahlbaum's, "aus Petroleum." When carbinol is used as the consolute liquid the plait points lie so near the paraffine end of the graphs that tie line measurements are impossible. This means that the tie lines radiate from the origin and that hence all the solutions obtained by adding carbinol to any mixture whatever of hexane or heptane and water, are in equilibrium with practically pure hexane. To check this conclusion the following measurements of the refractive index were made:

(1) Three cc of hexane, 3 cc of carbinol, and one drop water were shaken well together, let stand to separate and the top layer (about 2 cc) was then transferred to the cylinder of the refractometer and its index of refraction determined.

(2) Five cc of hexane, 7 cc of carbinol and 4 drops water, treated as before. The top layer was approximately 3 cc. The refractive index of both top and bottom layers was determined. Upper layer $\mu_{14} = 1.38343$, lower layer $\mu_{14} = 1.33935$.

(3) Three cc of hexane, 1 cc of water, well shaken and separated by centrifuging, upper layer $\mu_{14} = 1.38381$.

(4) Three cc. of hexane and an excess (about 2 drops) of carbinol, allowed to settle. Used the clear solution. $\mu_{14} = 1.38334$.

The refractometer used (Pulfrich's "Refractometer für Chemiker") gave as the value of μ_{14} for distilled water at 14° C. 1.33295 as against 1.33232 given in the Landolt-Bornstein tables; for benzene it gave 1.50139 as against 1.50137 in the tables; pure hexane gave 1.38382 and carbinol 1.33070, all at 14° C.

(34) Plait point is about water 0.02, alcohol 0.38.

(36) Through an oversight no tie line measurements were made:

Plait point between water 0.35 and 0.50:

(37) In this case (as also in the cases of experiments numbered 4, 8, 28, 35, 39, 41, 43 and 49) while the xylene is at first the upper layer, after the addition of a small amount of alcohol, the xylene layer sinks through the watery layer and becomes the lower. This gives another method of obtaining approximately the tie lines in these mixtures. Just before the point at which the "top" layer becomes the "bottom" there is a point at which the densities of the two are identical and the density of either is the density of the total mixture. Add alcohol until the "top" layer just begins to sink into the "bottom" and determine the density of the total mixture at this point. The tie line will be represented by a line passing through the point which gives the composition of the system and cutting the binodal curve at a point on either side which has the density of the given system. The last tie line in the table above was obtained in this way.

The composition of the system was water 0.295, alcohol 0.740, density 0.89.

(38) The plait point lies to the right of the point water 0.010.

(43) The first tie line is a first approximation only. Kahlbaum's best preparation, fractionated twice, b. p. 195°.

(44) The sample of *o*-nitrotoluene was prepared in the laboratory, b. p. 223°–224°.

(45) B. p. 199°.

It was impossible to get a satisfactory tie line measurement because the layers would not separate well enough to enable one to read the volumes, even up to the point where one drop of alcohol made the mixture homogeneous.

The plait point comes between 0.50 and 0.60.

(46) Kahlbaum's preparation, slightly discolored. Boiled with calcium turnings under reflux and fractionated. B. p. 107°–109°. The solubility of water in isobutyl alcohol at zero is 2.17 g water in 10 g and that of isobutyl alcohol in water is 1.15 g in 10 g water. The solubility decreases with rise of temperature.

(47) Kahlbaum's preparation free from pyridine. Dried over calcium turnings and distilled. B. p. 130°. The solubility in water at zero is 0.42 g in 10 g water and the solubility of water in isoamyl alcohol at zero is 0.81 g in 10 g alcohol.

TABLE V

(1) ether alcohol

Water	Alcohol	Density
0.041	0.161	0.78
0.087	0.224	0.79
*0.10	0.28	0.80
0.186	0.299	0.82
*0.20	0.305	0.82
0.299	0.354	0.85
0.399	0.376	0.86
P. P. 0.49	0.38	0.88
*0.50	0.39	0.88
0.586	0.381	0.90
*0.60	0.38	0.91
*0.70	0.37	0.93
0.712	0.365	0.93
*0.80	0.34	0.95
0.826	0.331	0.96
0.875	0.238	0.97
*0.90	0.16	0.97

Tie-lines

Water	Water
0.86	0.02
0.81	0.12
0.77	0.18
0.68	0.30
0.61	0.38

(2) chloroform alcohol

Water	Alcohol	Density
0.093	0.434	1.19
*0.10	0.45	1.18
0.185	0.587	1.13
*0.20	0.60	1.12
*0.30	0.68	1.07
0.317	0.692	1.06
0.407	0.726	1.04
0.499	0.729	1.03
P. P. 0.58	0.73	—
0.596	0.733	1.01
0.689	0.710	0.99
*0.70	0.70	0.99
0.803	0.672	0.98
*0.90	0.61	0.98
0.912	0.608	0.98
—	—	—
—	—	—

Tie-lines

Water	Water
0.10	0.97
0.22	0.90
0.43	0.72

(1) Logarithmic coördinates

Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$
0.10	$\bar{1}.638$	0.593
0.20	0.810	0.412
0.30	0.933	0.301
0.40	0.034	0.210
0.50	0.108	0.108
0.60	0.198	0.022
0.70	0.277	$\bar{1}.909$
0.80	0.372	$\bar{1}.770$
0.90	0.750	$\bar{1}.796$
P. P. —	0.565	$\bar{1}.720$

(2) Logarithmic coördinates

Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$
0.10	$\bar{1}.347$	0.301
0.20	0.523	0.125
0.30	0.645	0.013
0.40	0.742	$\bar{1}.918$
0.50	0.836	$\bar{1}.836$
0.60	0.913	$\bar{1}.737$
0.70	0.000	$\bar{1}.632$
0.80	0.076	$\bar{1}.474$
0.90	0.169	$\bar{1}.215$
P. P. —	$\bar{1}.900$	$\bar{1}.760$

TABLE V—(*Continued*)

(3) chloroform carbinol

Water	Carbinol	Density
0.021	0.161	—
*0.10	0.35	1.17
0.132	0.400	1.16
*0.20	0.49	1.12
P. P. 0.27	0.57	—
0.276	0.572	1.09
*0.30	0.60	1.08
0.368	0.666	1.07
*0.40	0.70	1.05
*0.50	0.77	1.02
0.519	0.783	1.01
*0.60	0.83	1.00
0.628	0.843	0.99
*0.70	0.86	0.98
*0.80	0.84	0.97
0.822	0.834	0.97
*0.90	0.74	0.96
0.943	0.622	—
0.987	0.267	0.98

(4) chloroform propyl alcohol

Water	Propyl alcohol	Density
0.023	0.304	1.28
0.074	0.631	1.13
*0.10	0.76	1.11
*0.20	1.06	1.04
0.240	1.128	1.02
*0.30	1.20	1.01
0.346	1.250	1.02
*0.40	1.30	0.98
*0.50	1.34	0.97
0.511	1.340	0.96
0.606	1.320	0.98
0.707	1.235	0.96
0.806	0.996	0.95
0.903	0.672	0.97
0.970	0.390	0.97
—	—	—
—	—	—
—	—	—
—	—	—

Tie-lines

Water	Water
0.00	0.70
0.01	0.58
0.03	0.55
0.05	0.51
0.11	0.45

Tie-lines

Water	Water
0.10	1.00
0.13	1.00
0.24	1.00
0.27	1.00
—	—

(3) Logarithmic coördinates

Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$
0.10	$\bar{1}.456$	0.410
0.20	$\bar{1}.611$	0.213
0.30	$\bar{1}.699$	0.067
0.40	$\bar{1}.757$	$\bar{1}.933$
0.50	$\bar{1}.813$	$\bar{1}.813$
0.60	$\bar{1}.859$	$\bar{1}.683$
0.70	$\bar{1}.911$	$\bar{1}.543$
0.80	$\bar{1}.979$	$\bar{1}.377$
0.90	$\bar{1}.085$	$\bar{1}.131$
P. P. —	$\bar{1}.676$	0.107

(4) Logarithmic coördinates

Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$
0.10	$\bar{1}.119$	0.073
0.20	$\bar{1}.276$	$\bar{1}.878$
0.30	$\bar{1}.398$	$\bar{1}.766$
0.40	$\bar{1}.488$	$\bar{1}.664$
0.50	$\bar{1}.572$	$\bar{1}.572$
0.60	$\bar{1}.656$	$\bar{1}.482$
0.70	$\bar{1}.755$	$\bar{1}.387$
0.80	$\bar{1}.908$	$\bar{1}.305$
0.90	0.128	$\bar{1}.174$
—	—	—

TABLE V—(*Continued*)

(5) chloroform acetone

Water	Acetone	Density
0.012	0.501	1.18
0.087	1.221	1.02
*0.10	1.30	1.01
0.208	1.633	0.98
0.304	1.750	0.96
0.344	1.742	0.96
*0.40	1.77	0.95
0.481	1.738	0.94
*0.50	1.72	0.94
P. P. 0.58	1.65	—
0.592	1.630	0.93
*0.60	1.63	0.93
*0.70	1.53	0.94
0.737	1.483	0.95
0.800	1.321	0.95
0.900	1.144	0.97
0.982	0.464	0.98
—	—	—

Tie-lines

Water	Water
0.15	0.99
0.17	0.98
0.18	0.97
0.19	0.96
0.20	0.96
0.21	0.95
0.22	0.93
0.25	0.91
0.30	0.85
0.51	0.66

(5) Logarithmic coördinates

Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$
0.10	$\bar{2}.886$	$\bar{1}.840$
0.20	$\bar{1}.089$	$\bar{1}.691$
0.30	$\bar{1}.234$	$\bar{1}.602$
0.40	$\bar{1}.354$	$\bar{1}.530$
0.50	$\bar{1}.464$	$\bar{1}.464$
0.60	$\bar{1}.566$	$\bar{1}.390$
0.70	$\bar{1}.660$	$\bar{1}.292$
0.80	$\bar{1}.783$	$\bar{1}.180$
0.90	$\bar{1}.897$	$\bar{2}.943$
P. P. —	$\bar{1}.550$	$\bar{1}.406$

(6) carbontetrachloride carbinol

Water	Carbinol	Density
P. P. 0.015	0.215	—
0.026	0.328	1.30
*0.10	0.74	1.13
0.156	0.974	1.06
*0.20	1.10	1.04
0.235	1.208	1.03
*0.30	1.40	1.00
0.316	1.403	0.99
*0.40	1.68	0.97
0.490	1.700	0.95
*0.50	1.71	0.95
*0.60	1.77	0.93
0.702	1.825	0.93
*0.80	1.88	0.92
0.852	1.890	0.92
*0.90	1.90	0.92
0.951	1.870	0.91
0.974	1.045	0.93

Tie-lines

Water	Water
0.000	0.110
0.005	0.035

(6) Logarithmic coördinates

Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$
0.10	$\bar{1}.131$	0.085
0.20	$\bar{1}.260$	$\bar{1}.862$
0.30	$\bar{1}.331$	$\bar{1}.699$
0.40	$\bar{1}.403$	$\bar{1}.580$
0.50	$\bar{1}.466$	$\bar{1}.466$
0.60	$\bar{1}.530$	$\bar{1}.354$
0.70	$\bar{1}.583$	$\bar{1}.215$
0.80	$\bar{1}.630$	$\bar{1}.027$
0.90	$\bar{1}.675$	$\bar{2}.721$
P. P. —	$\bar{2}.844$	0.661

TABLE V—(*Continued*)

(7) carbontetrachloride alcohol

Water	Alcohol	Density
0.039	0.224	1.36
0.072	0.347	1.23
P. P. 0.08	0.39	—
*0.10	0.45	1.20
0.156	0.598	1.16
*0.20	0.67	1.15
0.238	0.746	1.10
*0.30	0.82	1.07
0.361	0.891	1.05
*0.040	0.94	1.03
0.501	1.040	1.00
0.518	1.046	0.97
*0.60	1.00	0.97
*0.70	1.11	0.96
0.750	1.105	0.95
*0.80	1.10	0.94
0.887	1.104	0.95
*0.90	1.00	0.92
0.945	0.850	0.91
0.955	0.838	0.92
0.968	0.745	0.93

(8) carbontetrachloride propyl alcohol

Water	Propyl alcohol	Density
0.025	0.317	1.31
0.069	0.536	1.17
*0.10	0.65	1.14
0.200	0.949	1.07
0.270	1.070	1.03
*0.30	1.12	1.02
0.40	1.20	0.99
0.414	1.208	0.99
0.501	1.234	0.98
0.600	1.195	0.97
*0.70	1.13	0.96
0.710	1.119	0.96
P. P. 0.75	1.06	—
0.806	0.912	0.96
*0.90	0.68	0.96
0.911	0.645	0.96
0.987	0.354	0.96
—	—	—
—	—	—
—	—	—
—	—	—

Tie-lines

Water	Water
0.01	0.30
0.02	0.22
0.03	0.16
0.05	0.13

Tie-lines

Water	Water
0.21	0.99
0.47	1.00
0.56	0.99
0.52	0.90

(7) Logarithmic coördinates

Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$
0.10	$\bar{1}.347$	0.301
0.20	$\bar{1}.475$	0.077
0.30	$\bar{1}.567$	$\bar{1}.931$
0.40	$\bar{1}.629$	$\bar{1}.805$
0.50	$\bar{1}.683$	$\bar{1}.683$
0.60	$\bar{1}.741$	$\bar{1}.565$
0.70	$\bar{1}.800$	$\bar{1}.432$
0.80	$\bar{1}.863$	$\bar{1}.260$
0.90	$\bar{1}.954$	$\bar{1}.000$
P. P. —	$\bar{1}.312$	0.373

(8) Logarithmic coördinates

Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$
0.10	$\bar{1}.187$	0.141
0.20	$\bar{1}.330$	$\bar{1}.930$
0.30	$\bar{1}.428$	$\bar{1}.796$
0.40	$\bar{1}.523$	$\bar{1}.699$
0.50	$\bar{1}.609$	$\bar{1}.609$
0.60	$\bar{1}.699$	$\bar{1}.523$
0.70	$\bar{1}.792$	$\bar{1}.424$
0.80	$\bar{1}.944$	$\bar{1}.342$
0.90	0.121	$\bar{1}.168$
P. P. —	$\bar{1}.850$	$\bar{1}.373$

TABLE V—(*Continued*)

(9) ethylene chloride alcohol

Water	Alcohol	Density
0.029	0.191	1.15
0.050	0.266	1.12
*0.10	0.42	1.08
P. P. 0.12	0.46	—
0.208	0.670	1.01
0.290	0.789	0.98
*0.30	0.80	0.98
*0.40	0.93	0.96
0.486	0.983	0.95
*0.50	0.99	0.95
0.580	1.000	0.95
*0.60	1.01	0.94
*0.70	0.99	0.94
0.790	0.958	0.94
*0.80	0.95	0.94
0.905	0.842	0.96
0.980	0.514	0.97
—	—	—

Tie-lines

Water	Water
0.00	0.48
0.01	0.36
0.03	0.22

(9) Logarithmic coördinates

Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$
0.10	$\bar{1}.377$	0.331
0.20	$\bar{1}.475$	0.077
0.30	$\bar{1}.574$	$\bar{1}.942$
0.40	$\bar{1}.634$	$\bar{1}.810$
0.50	$\bar{1}.703$	$\bar{1}.703$
0.60	$\bar{1}.774$	$\bar{1}.598$
0.70	$\bar{1}.850$	$\bar{1}.482$
0.80	$\bar{1}.925$	$\bar{1}.323$
0.90	0.029	$\bar{1}.076$
P. P. —	0.416	0.282

(10) ethylidene chloride alcohol

Water	Alcohol	Density
0.015	0.226	1.10
*0.10	0.43	1.03
0.109	0.436	1.02
0.195	0.586	1.01
*0.30	0.69	0.98
0.316	0.705	1.00
P. P. 0.33	0.72	—
*0.40	0.77	0.96
0.423	0.770	0.96
*0.50	0.82	0.95
0.563	0.857	0.94
0.667	0.87	0.94
*0.70	0.88	0.93
0.765	0.864	0.93
*0.80	0.86	0.93
*0.90	0.79	0.94
0.910	0.774	0.94
0.970	0.576	0.95

Tie-lines

Water	Water
0.00	0.79
0.01	0.77
0.03	0.70
0.11	0.61
0.20	0.47

(10) Logarithmic coördinates

Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$
0.10	$\bar{1}.367$	0.321
0.20	$\bar{1}.533$	0.135
0.30	$\bar{1}.638$	0.006
0.40	$\bar{1}.716$	$\bar{1}.892$
0.50	$\bar{1}.785$	$\bar{1}.785$
0.60	$\bar{1}.839$	$\bar{1}.663$
0.70	$\bar{1}.901$	$\bar{1}.533$
0.80	$\bar{1}.969$	$\bar{1}.367$
0.90	0.057	$\bar{1}.102$
P. P. —	$\bar{1}.661$	$\bar{1}.969$

TABLE V—(*Continued*)

(11) ethyl bromide carbinol

Water	Carbinol	Density
0.027	0.202	1.27
P. P. 0.05	0.33	—
0.064	0.393	1.18
*0.10	0.54	1.14
0.194	0.868	1.08
*0.20	0.86	1.05
0.291	1.023	1.01
*0.30	1.04	1.01
0.398	1.180	1.00
*0.40	1.18	0.99
0.498	1.250	0.97
*0.50	1.26	0.97
0.600	1.310	0.96
*0.70	1.29	0.95
0.750	1.270	0.95
*0.80	1.21	0.94
0.816	1.100	0.95
*0.90	0.94	0.94
0.919	0.870	0.94
0.978	0.194	0.98

(12) ethyl bromide alcohol

Water	Alcohol	Density
0.033	0.240	1.23
*0.10	0.37	1.15
P. P. 0.17	0.45	—
0.189	0.493	1.09
*0.20	0.51	1.09
*0.30	0.64	1.06
0.365	0.720	1.04
*0.40	0.754	1.03
0.476	0.807	1.01
*0.50	0.83	1.00
*0.60	0.89	0.99
0.657	0.900	0.98
*0.70	0.89	0.97
*0.80	0.83	0.96
0.837	0.797	0.96
*0.90	0.73	0.97
0.948	0.623	0.98
0.983	0.182	0.99
—	—	—
—	—	—

Tie-lines

Water	Water
0.00	0.21
0.01	0.14
0.02	0.11
0.02	0.08

Tie-lines

Water	Water
0.00	0.63
0.01	0.46
0.06	0.27

(11) Logarithmic coördinates

Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$
0.10	$\bar{1}.268$	0.222
0.20	$\bar{1}.367$	$\bar{1}.969$
0.30	$\bar{1}.460$	$\bar{1}.828$
0.40	$\bar{1}.530$	$\bar{1}.706$
0.50	$\bar{1}.599$	$\bar{1}.599$
0.60	$\bar{1}.661$	$\bar{1}.485$
0.70	$\bar{1}.735$	$\bar{1}.367$
0.80	$\bar{1}.820$	$\bar{1}.218$
0.90	$\bar{1}.981$	0.027
P. P. —	$1.\bar{1}81$	0.459

(12) Logarithmic coördinates

Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$
0.10	$\bar{1}.432$	0.386
0.20	$\bar{1}.593$	0.196
0.30	$\bar{1}.671$	0.039
0.40	$\bar{1}.727$	$\bar{1}.903$
0.50	$\bar{1}.780$	$\bar{1}.780$
0.60	$\bar{1}.829$	$\bar{1}.653$
0.70	$\bar{1}.896$	$\bar{1}.527$
0.80	$\bar{1}.984$	$\bar{1}.382$
0.90	0.091	$\bar{1}.137$
P. P. —	$\bar{1}.577$	0.266

TABLE V—(*Continued*)

(13) ethyl bromide propyl alcohol

Water	Propyl alcohol	Density
0.039	0.367	1.21
0.088	0.615	1.11
*0.10	0.64	1.10
*0.20	0.85	1.05
0.215	0.800	1.05
*0.30	1.00	1.02
0.334	1.061	1.03
*0.40	1.09	1.00
0.413	1.092	1.01
0.509	1.124	0.98
0.584	1.115	0.96
*0.60	1.10	0.97
0.694	0.998	0.97
*0.70	0.90	0.96
0.80	0.81	0.96
0.860	0.671	0.96
*0.90	0.56	0.97
0.977	0.227	0.99
—	—	—

(14) propyl bromide alcohol

Water	Alcohol	Density
0.025	0.190	1.26
P. P. 0.08	0.42	—
*0.10	0.50	1.12
0.107	0.508	1.12
*0.20	0.72	1.06
0.231	0.700	1.04
*0.30	0.88	1.02
0.328	0.920	1.01
*0.40	1.01	0.99
0.432	1.181	1.00
0.496	1.096	0.98
*0.50	1.10	0.98
0.563	1.134	0.96
*0.60	1.15	0.96
0.695	1.140	0.95
*0.70	1.14	0.95
0.796	1.120	0.94
0.904	1.020	0.94
0.973	0.687	0.95

Tie-lines

Water	Water
0.00	0.96
0.00	0.80
0.00	0.53
0.00	0.34
0.01	0.27
0.02	0.21
0.03	0.16
0.04	0.14

(13) Logarithmic coördinates

Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$
0.10	$\bar{1}.194$	0.148
0.20	$\bar{1}.372$	$\bar{1}.974$
0.30	$\bar{1}.477$	$\bar{1}.845$
0.40	$\bar{1}.565$	$\bar{1}.741$
0.50	$\bar{1}.650$	$\bar{1}.650$
0.60	$\bar{1}.737$	$\bar{1}.561$
0.70	$\bar{1}.850$	$\bar{1}.482$
0.80	$\bar{1}.995$	$\bar{1}.393$
0.90	0.200	$\bar{1}.252$
—	—	—

(14) Logarithmic coördinates

Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$
0.10	$\bar{1}.301$	0.255
0.20	$\bar{1}.444$	0.046
0.30	$\bar{1}.533$	$\bar{1}.901$
0.40	$\bar{1}.598$	$\bar{1}.774$
0.50	$\bar{1}.658$	$\bar{1}.658$
0.60	$\bar{1}.718$	$\bar{1}.541$
0.70	$\bar{1}.788$	$\bar{1}.420$
0.80	$\bar{1}.854$	$\bar{1}.252$
0.90	$\bar{1}.946$	$\bar{2}.991$
P. P.	$\bar{1}.280$	0.341

TABLE V—(*Continued*)

(15) isobutyl bromide alcohol

Water	Alcohol	Density
0.024	0.200	1.18
P. P. 0.07	0.42	—
*0.10	0.52	1.09
0.124	0.607	1.06
*0.20	0.83	1.01
0.218	0.887	1.00
0.293	1.039	0.98
*0.30	1.05	0.98
0.386	1.194	0.96
*0.40	1.21	0.96
0.499	1.300	0.94
0.598	1.359	0.93
*0.60	1.35	0.93
0.696	1.356	0.93
*0.70	1.36	0.93
*0.80	1.32	0.92
0.804	1.316	0.92
0.896	1.215	0.93
*0.90	1.20	0.93
0.953	0.937	0.94

Tie-lines

Water	Water
0.00	0.51
0.00	0.24
0.03	0.13

(15) Logarithmic coördinates

Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$
0.10	$\bar{1}.284$	0.238
0.20	$\bar{1}.382$	$\bar{1}.984$
0.30	$\bar{1}.456$	$\bar{1}.824$
0.40	$\bar{1}.519$	$\bar{1}.695$
0.50	$\bar{1}.586$	$\bar{1}.586$
0.60	$\bar{1}.648$	$\bar{1}.472$
0.70	$\bar{1}.712$	$\bar{1}.344$
0.80	$\bar{1}.783$	$\bar{1}.180$
0.90	$\bar{2}.875$	$\bar{2}.920$
P. P. —	$\bar{1}.222$	0.545

(16) isoamyl bromide alcohol

Water	Alcohol	Density
0.025	0.251	1.10
P. P. 0.04	0.36	—
0.189	0.636	1.01
*0.10	0.68	1.01
*0.20	1.09	0.96
0.223	1.178	0.97
*0.30	1.37	0.94
0.324	1.432	0.93
*0.40	1.57	0.93
0.414	1.594	0.93
0.502	1.676	0.91
0.583	1.744	0.91
*0.60	1.75	0.91
0.692	1.747	—
*0.70	1.75	0.91
*0.80	1.71	0.91
0.809	1.713	0.91
0.895	1.463	0.92
*0.90	1.46	0.92
0.978	1.027	0.93

Tie-lines

Water	Water
0.00	0.43
0.01	0.11
0.02	0.06

(16) Logarithmic coördinates

Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$
0.10	$\bar{1}.168$	0.122
0.20	$\bar{1}.264$	$\bar{1}.866$
0.30	$\bar{1}.340$	$\bar{1}.708$
0.40	$\bar{1}.406$	$\bar{1}.582$
0.50	$\bar{1}.476$	$\bar{1}.476$
0.60	$\bar{1}.535$	$\bar{1}.359$
0.70	$\bar{1}.602$	$\bar{1}.234$
0.80	$\bar{1}.670$	$\bar{1}.068$
0.90	$\bar{1}.790$	$\bar{2}.836$
P. P. —	$\bar{1}.049$	0.426

TABLE V—(*Continued*)

(17) brombenzene carbinol

Water	Carbinol	Density
0.009	0.230	—
0.015	0.314	1.24
P. P. 0.02	0.40	—
0.031	0.453	1.16
*0.10	1.01	1.04
0.127	1.170	1.01
0.198	1.491	0.98
*0.20	1.50	0.98
0.237	1.751	0.96
*0.30	1.84	0.95
0.357	1.932	0.93
0.400	2.065	0.94
*0.50	2.24	0.91
0.551	2.290	0.90
*0.60	2.30	0.90
0.633	2.295	0.90
*0.70	2.28	0.89
*0.80	2.20	0.89
0.812	2.185	0.91
0.905	1.927	0.90
0.984	1.332	0.91

Tie-lines

Water	Water
0.00	0.07

(18) brombenzene alcohol

Water	Alcohol	Density
0.010	0.115	1.34
P. P. 0.04	0.32	—
*0.10	0.65	1.07
0.109	0.641	1.09
0.195	0.988	0.96
*0.20	1.00	0.96
*0.30	1.19	0.96
0.354	1.240	0.97
*0.40	1.30	0.98
0.414	1.326	0.98
0.498	1.385	—
*0.50	1.39	0.95
0.593	1.420	0.91
*0.60	1.43	0.91
0.695	1.434	0.90
*0.70	1.43	0.92
*0.80	1.36	0.93
0.840	1.305	0.92
*0.90	1.16	0.93
0.903	1.150	0.94
0.976	0.803	0.92

Tie-lines

Water	Water
0.00	0.22
0.00	0.16
0.01	0.09
0.02	0.06

(17) Logarithmic coördinates

Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$
0.10	$\bar{2}.996$	$\bar{1}.950$
0.20	$\bar{1}.125$	$\bar{1}.727$
0.30	$\bar{1}.212$	$\bar{1}.580$
0.40	$\bar{1}.287$	$\bar{1}.463$
0.50	$\bar{1}.349$	$\bar{1}.349$
0.60	$\bar{1}.416$	$\bar{1}.240$
0.70	$\bar{1}.487$	$\bar{1}.119$
0.80	$\bar{1}.560$	$\bar{2}.958$
0.90	$\bar{1}.669$	$\bar{2}.714$
P. P. —	$\bar{2}.699$	0.389

(18) Logarithmic coördinates

Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$
0.10	$\bar{1}.187$	0.141
0.20	$\bar{1}.301$	$\bar{1}.903$
0.30	$\bar{1}.402$	$\bar{1}.770$
0.40	$\bar{1}.488$	$\bar{1}.664$
0.50	$\bar{1}.556$	$\bar{1}.556$
0.60	$\bar{1}.623$	$\bar{1}.447$
0.70	$\bar{1}.690$	$\bar{1}.322$
0.80	$\bar{1}.770$	$\bar{1}.168$
0.90	$\bar{1}.890$	$\bar{2}.935$
P. P. —	$\bar{1}.097$	0.477

TABLE V—(*Continued*)

(19) brombenzene propyl alcohol

Water	Alcohol	Density
0.017	0.186	1.29
0.091	0.560	1.11
*0.10	0.58	1.11
*0.20	0.87	1.05
0.230	0.936	1.04
*0.30	1.05	1.02
0.358	1.110	1.01
*0.40	1.15	1.00
*0.50	1.19	0.97
0.512	1.195	0.97
0.573	1.208	0.97
*0.60	1.19	0.96
*0.70	1.09	0.95
0.708	1.071	0.95
*0.80	0.93	0.95
0.815	0.899	—
*0.90	0.71	0.96
0.906	0.687	0.96
0.979	0.457	0.98
—	—	—

Tie-lines

Water	Water
0.35	1.00
0.54	1.00
0.51	0.99
0.33	0.77

(19) Logarithmic coördinates

Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$
0.10	$\bar{1}.237$	0.191
0.20	$\bar{1}.362$	$\bar{1}.964$
0.30	$\bar{1}.456$	$\bar{1}.824$
0.40	$\bar{1}.541$	$\bar{1}.718$
0.50	$\bar{1}.624$	$\bar{1}.624$
0.60	$\bar{1}.703$	$\bar{1}.527$
0.70	$\bar{1}.808$	$\bar{1}.440$
0.80	$\bar{1}.935$	$\bar{1}.333$
0.90	0.103	$\bar{1}.149$
—	—	—

(20) brombenzene acetone

Water	Acetone	Density
0.023	0.685	1.12
*0.10	1.13	1.01
0.107	1.175	1.01
*0.20	1.41	0.98
0.236	1.470	1.00
*0.30	1.52	0.97
0.319	1.535	0.96
*0.40	1.57	0.96
0.402	1.570	0.96
*0.50	1.60	0.95
P. P. 0.51	1.60	—
0.547	1.600	0.95
*0.60	1.59	0.94
*0.70	1.55	0.93
0.715	1.540	0.94
0.792	1.454	0.93
*0.80	1.46	0.93
0.874	1.365	0.93
*0.90	1.30	0.93
0.980	0.849	0.95

Tie-lines

Water	Water
0.11	0.94
0.15	0.86
0.29	0.73
0.38	0.64

(20) Logarithmic coördinates

Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$
0.10	$\bar{2}.947$	$\bar{1}.901$
0.20	$\bar{1}.152$	$\bar{1}.754$
0.30	$\bar{1}.295$	$\bar{1}.663$
0.40	$\bar{1}.406$	$\bar{1}.582$
0.50	$\bar{1}.495$	$\bar{1}.495$
0.60	$\bar{1}.577$	$\bar{1}.400$
0.70	$\bar{1}.655$	$\bar{1}.287$
0.80	$\bar{1}.739$	$\bar{1}.137$
0.90	$\bar{1}.840$	$\bar{2}.886$
P. P. —	$\bar{1}.504$	$\bar{1}.486$

TABLE V—(*Continued*)

(21) bromtoluene carbinol (22) bromtoluene alcohol

Water	Alcohol	Density
0.02	0.33	—
0.049	0.522	1.09
*0.10	0.87	1.06
0.146	1.086	1.01
*0.20	1.28	0.97
0.232	1.352	0.95
*0.30	1.54	0.94
0.386	1.700	—
*0.40	1.71	0.93
*0.50	1.81	0.92
0.534	1.850	0.92
*0.60	1.89	0.91
0.620	1.900	0.91
*0.70	1.89	0.90
0.785	1.800	0.91
*0.80	1.78	0.90
0.900	1.533	0.91
0.967	1.307	0.92

Tie-lines

Water	Water
0.00	0.13
0.00	0.10
0.00	0.07
0.01	0.06

(22) Logarithmic coördinates

Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$
0.10	$\bar{1}.061$	0.015
0.20	$\bar{1}.194$	$\bar{1}.796$
0.30	$\bar{1}.290$	$\bar{1}.658$
0.40	$\bar{1}.369$	$\bar{1}.545$
0.50	$\bar{1}.441$	$\bar{1}.441$
0.60	$\bar{1}.502$	$\bar{1}.326$
0.70	$\bar{1}.569$	$\bar{1}.201$
0.80	$\bar{1}.653$	$\bar{1}.041$
0.90	$\bar{1}.770$	$\bar{2}.815$
P. P. —	$\bar{2}.783$	0.473

TABLE V—(*Continued*)

(23) bromtoluene propyl alcohol

Water	Alcohol	Density
0.032	0.252	1.23
*0.10	0.52	1.11
0.104	0.529	1.10
0.188	0.755	1.04
*0.20	0.78	1.03
0.30	0.96	1.01
0.303	0.955	1.01
*0.40	1.07	0.99
0.407	1.075	0.99
0.496	1.127	0.98
*0.50	1.13	0.97
0.560	1.124	0.96
0.598	1.139	0.96
*0.60	1.13	0.96
0.677	1.075	0.95
*0.70	1.03	0.95
P. P. 0.75	0.97	—
0.797	0.909	0.94
*0.80	0.90	0.94
*0.90	0.72	0.95
0.925	0.660	0.95
0.987	0.424	0.96

Tie-lines

Water	Water
0.19	0.99
0.33	0.99
0.43	0.99
0.52	0.92

(23) Logarithmic coördinates

Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$
0.10	$\bar{1}.284$	0.238
0.20	$\bar{1}.409$	0.011
0.30	$\bar{1}.495$	$\bar{1}.863$
0.40	$\bar{1}.573$	$\bar{1}.749$
0.50	$\bar{1}.646$	$\bar{1}.646$
0.60	$\bar{1}.725$	$\bar{1}.549$
0.70	$\bar{1}.832$	$\bar{1}.464$
0.80	$\bar{1}.949$	$\bar{1}.347$
0.90	0.097	$\bar{1}.143$
P. P. —	$\bar{1}.888$	$\bar{1}.411$

(24) ethyl acetate alcohol

Water	Alcohol	Density
0.080	0.100	0.91
*0.10	0.13	0.91
0.201	0.228	0.93
0.203	0.222	0.93
0.301	0.265	0.92
0.396	0.290	0.95
*0.40	0.29	0.95
0.50	0.30	0.95
0.507	0.297	0.94
P. P. 0.52	0.30	—
*0.60	0.31	0.96
0.611	0.310	0.96
0.689	0.304	0.96
*0.70	0.31	0.96
0.803	0.282	0.97
0.898	0.143	0.99
—	—	—
—	—	—
—	—	—
—	—	—
—	—	—
—	—	—

Tie-lines

Water	Water
0.88	0.05
0.86	0.15
0.78	0.20
0.73	0.30

(24) Logarithmic coördinates

Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$
0.10	$\bar{1}.886$	0.840
0.20	$\bar{1}.943$	0.545
0.30	0.054	0.422
0.40	0.140	0.316
0.50	0.222	0.222
0.60	0.287	0.110
0.70	0.354	$\bar{1}.986$
0.80	0.456	$\bar{1}.854$
0.90	0.799	$\bar{1}.845$
P. P. —	0.239	0.204

TABLE V—(*Continued*)

(25) benzyl acetate alcohol

Water	Alcohol	Density
0.023	0.120	1.05
0.099	0.317	1.03
0.197	0.459	0.97
*0.20	0.46	0.99
*0.30	0.58	0.97
0.38	0.601	0.96
P. P. 0.32	0.60	—
*0.40	0.69	0.95
0.415	0.705	0.95
0.489	0.770	0.95
*0.50	0.78	0.94
0.593	0.841	0.94
*0.60	0.85	0.94
0.700	0.880	0.93
0.781	0.883	—
*0.80	0.88	0.93
0.888	0.818	0.94
*0.90	0.80	0.94
0.959	0.665	0.95

Tie-lines

Water	Water
0.00	0.93
0.03	0.73
0.11	0.58
0 17	0.47

(26) ethyl propionate alcohol

Water	Alcohol	Density
0.023	0.138	0.90
0.085	0.257	0.91
*0.10	0.27	0.90
0.102	0.373	0.90
*0.20	0.38	0.90
0.305	0.453	0.92
*0.40	0.49	0.91
0.494	0.520	0.92
*0.50	0.52	0.92
P. P. 0.54	0.53	—
0.602	0.532	0.93
0.698	0.547	0.94
*0.70	0.55	0.94
0.799	0.517	0.95
*0.90	0.46	0.96
0.914	0.443	0.97
—	—	—
—	—	—
—	—	—

Tie-lines

Water	Water
0.95	0.02
0.92	0.13
0.86	0.14
0.83	0.24
0.76	0.34
0.67	0.41

(25) Logarithmic coördinates

Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$
0.10	$\bar{1}.499$	0.453
0.20	$\bar{1}.638$	0.240
0.30	$\bar{1}.714$	0.082
0.40	$\bar{1}.763$	$\bar{1}.939$
0.50	$\bar{1}.807$	$\bar{1}.807$
0.60	$\bar{1}.849$	$\bar{1}.673$
0.70	$\bar{1}.901$	$\bar{1}.533$
0.80	$\bar{1}.959$	$\bar{1}.356$
0.90	0.051	$\bar{1}.097$
P. P. —	$\bar{1}.727$	0.054

(26) Logarithmic coördinates

Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$
0.10	$\bar{1}.569$	0.523
0.20	$\bar{1}.721$	0.323
0.30	$\bar{1}.824$	0.192
0.40	$\bar{1}.912$	0.088
0.50	$\bar{1}.983$	$\bar{1}.983$
0.60	0.054	$\bar{1}.878$
0.70	0.105	$\bar{1}.737$
0.80	0.190	$\bar{1}.587$
0.90	0.291	$\bar{1}.337$
P. P. —	0.008	$\bar{1}.939$

TABLE V—(*Continued*)

(27) ethyl butyrate alcohol

Water	Alcohol	Density
0.030	0.166	0.90
0.097	0.314	0.90
*0.10	0.32	—
0.200	0.483	0.88
0.300	0.567	0.89
0.401	0.628	0.90
0.506	0.659	0.91
P. P. 0.54	0.67	—
0.598	0.684	0.92
*0.60	0.69	0.92
0.703	0.693	0.93
0.807	0.684	0.94
*0.90	0.63	0.94
0.910	0.603	0.95
—	—	—
—	—	—
—	—	—
—	—	—
—	—	—

(28) benzyl ethyl ether alcohol

Water	Alcohol	Density
0.029	0.189	0.94
*0.10	0.37	0.92
0.108	0.381	0.92
0.191	0.528	0.92
*0.20	0.54	0.92
0.274	0.648	0.92
*0.30	0.67	0.91
P. P. 0.33	0.71	—
*0.40	0.78	0.91
0.410	0.790	0.91
0.494	0.874	—
*0.50	0.87	0.91
0.594	0.930	0.92
*0.60	0.93	0.92
*0.70	0.96	0.92
0.711	0.960	0.92
0.802	0.952	0.92
*0.90	0.86	0.93
0.920	0.793	0.94

Tie-lines

Water	Water
0.96	0.00
0.93	0.05
0.89	0.11
0.81	0.25
0.72	0.36
0.62	0.45

Tie-lines

Water	Water
0.00	0.73
0.03	0.70
0.15	0.52

(27) Logarithmic coördinates

Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$
0.10	$\bar{1}.495$	0.449
0.20	$\bar{1}.617$	0.219
0.30	$\bar{1}.723$	0.091
0.40	$\bar{1}.804$	$\bar{1}.980$
0.50	$\bar{1}.880$	$\bar{1}.880$
0.60	0.939	$\bar{1}.763$
0.70	0.004	$\bar{1}.636$
0.80	0.008	$\bar{1}.475$
0.90	0.155	$\bar{1}.201$
P. P. —	$\bar{1}.906$	$\bar{1}.837$

(28) Logarithmic coördinates

Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$
0.10	$\bar{1}.432$	0.386
0.20	$\bar{1}.569$	0.171
0.30	$\bar{1}.651$	0.019
0.40	$\bar{1}.710$	$\bar{1}.886$
0.50	$\bar{1}.759$	$\bar{1}.759$
0.60	$\bar{1}.810$	$\bar{1}.634$
0.70	$\bar{1}.863$	$\bar{1}.495$
0.80	$\bar{1}.924$	$\bar{1}.322$
0.90	0.020	$\bar{1}.065$
P. P. —	$\bar{1}.667$	$\bar{1}.975$

TABLE V—(*Continued*)

(29) isoamyl ether alcohol

Water	Alcohol	Density
0.042	0.368	0.81
*0.10	0.70	0.82
P. P. 0.11	0.74	—
0.121	0.793	0.82
*0.20	1.20	0.83
0.233	1.324	0.83
0.298	1.573	0.83
0.406	1.876	0.84
*0.50	1.98	0.84
0.590	2.188	0.85
*0.60	2.19	0.85
0.698	2.240	0.86
*0.80	2.14	0.87
0.819	2.102	0.88
*0.90	1.87	0.89
0.914	1.792	0.89

(30) diethyl ketone alcohol

Water	Alcohol	Density
0.062	0.136	0.85
*0.10	0.19	0.85
0.105	0.201	0.86
*0.20	0.31	0.87
0.219	0.317	0.87
0.298	0.356	0.88
0.400	0.392	0.89
0.453	0.410	0.90
0.501	0.411	0.91
0.542	0.415	0.92
0.593	0.404	0.91
—	—	—
—	—	—
—	—	—
—	—	—
—	—	—

Tie-lines

Water	Water
0.72	0.00
0.50	0.00
0.28	0.00
0.24	0.01
0.21	0.02
0.19	0.03

(30) Logarithmic coördinates

Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$
0.10	$\bar{1}.721$	0.675
0.20	$\bar{1}.810$	0.412
0.30	$\bar{1}.921$	0.289
0.40	0.008	0.185
0.50	0.085	0.085
0.60	0.167	0.004

(29) Logarithmic coördinates

Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$
0.10	$\bar{1}.174$	0.129
0.20	$\bar{1}.222$	$\bar{1}.824$
0.30	$\bar{1}.281$	$\bar{1}.649$
0.40	$\bar{1}.330$	$\bar{1}.506$
0.50	$\bar{1}.402$	$\bar{1}.402$
0.60	$\bar{1}.438$	$\bar{1}.262$
0.70	$\bar{1}.495$	$\bar{1}.127$
0.80	$\bar{1}.573$	$\bar{2}.971$
0.90	$\bar{1}.682$	$\bar{2}.728$
P. P. —	$\bar{1}.172$	0.080

TABLE V—(*Continued*)

(31) hexane carbinol

Water	Carbinol	Density
0.067	4.280	—
*0.10	4.69	0.80
0.160	5.090	0.80
*0.20	5.26	0.80
0.309	5.710	0.82
*0.40	6.17	0.81
0.414	6.240	0.82
0.509	6.365	0.83
*0.60	6.33	0.83
0.652	6.241	0.83
0.670	6.222	—
*0.70	6.13	0.84
0.80	5.49	0.85
0.830	5.012	0.85
*0.90	4.01	0.86
0.905	3.912	0.87
0.984	1.759	0.91

(31) Logarithmic coördinates

Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$
0.10	$\bar{2}.329$	$\bar{1}.283$
0.20	$\bar{2}.580$	$\bar{1}.182$
0.30	$\bar{2}.720$	$\bar{1}.088$
0.40	$\bar{2}.812$	$\bar{2}.988$
0.50	$\bar{2}.896$	$\bar{2}.896$
0.60	$\bar{2}.977$	$\bar{2}.801$
0.70	$\bar{1}.058$	$\bar{2}.690$
0.80	$\bar{1}.164$	$\bar{2}.551$
0.90	$\bar{1}.351$	$\bar{2}.397$

(32) hexane alcohol

Water	Alcohol	Density
P. P. 0.03	0.59	—
0.035	0.64	0.75
*0.10	1.30	0.77
0.134	1.64	0.79
0.173	1.899	0.79
*0.20	2.04	0.79
0.272	2.415	0.81
*0.30	2.45	0.81
0.389	2.712	0.82
*0.40	2.73	0.82
*0.50	2.93	0.83
0.525	2.960	0.83
0.575	3.000	0.83
*0.60	3.00	0.83
0.702	2.918	0.83
*0.80	2.75	0.85
0.815	2.720	0.86
0.895	2.278	0.86
*0.90	2.23	0.86
0.986	1.056	—

Tie-lines

Water	Water
0.11	0.00
0.07	0.00
0.05	0.01

TABLE V—(*Continued*)

(32) Logarithmic coördinates

Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$
0.10	$\bar{2}.886$	$\bar{1}.840$
0.20	$\bar{2}.991$	$\bar{1}.594$
0.30	$\bar{1}.088$	$\bar{1}.456$
0.40	$\bar{1}.166$	$\bar{1}.342$
0.50	$\bar{1}.232$	$\bar{1}.232$
0.60	$\bar{1}.301$	$\bar{1}.125$
0.70	$\bar{1}.383$	$\bar{1}.015$
0.80	$\bar{1}.464$	$\bar{2}.862$
0.90	$\bar{1}.606$	$\bar{2}.652$
P. P. —	$\bar{2}.706$	0.216

(33) heptane carbinol

Water	Carbinol	Density
0.034	4.78	—
*0.10	5.55	0.80
0.126	5.93	0.80
0.207	6.36	0.82
*0.30	7.30	0.82
0.321	7.46	0.82
0.400	8.22	0.82
*0.50	8.76	0.82
0.520	8.80	0.83
*0.60	8.65	0.83
0.672	8.05	0.83
*0.70	7.78	0.83
0.802	6.71	0.84
*0.90	4.40	0.87
0.962	2.96	0.91

(33) Logarithmic coördinates

Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$
0.10	$\bar{2}.256$	$\bar{1}.210$
0.20	$\bar{2}.497$	$\bar{1}.100$
0.30	$\bar{2}.614$	$\bar{2}.982$
0.40	$\bar{2}.687$	$\bar{2}.863$
0.50	$\bar{2}.757$	$\bar{2}.757$
0.60	$\bar{2}.841$	$\bar{2}.665$
0.70	$\bar{2}.954$	$\bar{2}.586$
0.80	$\bar{1}.076$	$\bar{2}.474$
0.90	$\bar{1}.311$	$\bar{2}.357$

(34) heptane alcohol

Water	Alcohol	Density
0.038	0.704	0.79
*0.10	1.44	0.80
0.118	1.685	0.80
0.202	2.375	0.82
*0.30	2.82	0.81
0.341	2.940	0.82
0.388	3.015	0.82
*0.40	3.06	0.82
*0.50	3.16	0.83
0.545	3.168	0.83
*0.60	3.17	0.84
*0.70	3.10	0.85
0.725	3.080	0.85
0.804	2.960	0.87
0.907	2.305	0.88

(34) Logarithmic coördinates

Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$
0.10	$\bar{2}.842$	$\bar{1}.796$
0.20	$\bar{2}.926$	$\bar{1}.528$
0.30	$\bar{1}.027$	$\bar{1}.395$
0.40	$\bar{1}.116$	$\bar{1}.293$
0.50	$\bar{1}.199$	$\bar{1}.199$
0.60	$\bar{1}.277$	$\bar{1}.101$
0.70	$\bar{1}.354$	$\bar{2}.986$
0.80	$\bar{1}.432$	$\bar{2}.830$
0.90	$\bar{1}.593$	$\bar{2}.638$

TABLE V—(*Continued*)

(35) benzene alcohol (temp. 15°)

Water	Alcohol	Density
0.013	0.170	0.86
0.063	0.356	0.87
P. P. 0.10	0.50	0.86
0.183	0.708	0.85
*0.20	0.86	0.86
0.298	0.917	0.88
*0.30	0.91	0.88
*0.40	1.07	0.87
0.409	1.080	0.87
*0.50	1.18	0.87
0.517	1.188	0.88
*0.60	1.22	0.88
0.614	1.200	0.88
0.681	1.210	0.89
*0.70	1.21	0.89
0.799	1.130	0.89
0.898	0.972	0.92
*0.90	0.97	0.92
0.980	0.590	0.94

Tie-lines

Water	Water
0.04	0.18

(35) Logarithmic coördinates

Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$
0.10	$\bar{1}.301$	0.255
0.20	$\bar{1}.438$	0.040
0.30	$\bar{1}.518$	$\bar{1}.886$
0.40	$\bar{1}.573$	$\bar{1}.749$
0.50	$\bar{1}.627$	$\bar{1}.627$
0.60	$\bar{1}.692$	$\bar{1}.516$
0.70	$\bar{1}.762$	$\bar{1}.394$
0.80	$\bar{1}.850$	$\bar{1}.248$
0.90	$\bar{1}.967$	$\bar{1}.013$
P. P. —	$\bar{1}.301$	0.255

(36) toluene alcohol

Water	Alcohol	Density
0.052	0.388	0.87
0.083	0.538	0.86
*0.10	0.61	0.86
0.121	0.705	0.86
*0.20	0.95	0.86
*0.30	1.21	0.86
0.351	1.323	0.86
*0.40	1.41	0.86
*0.50	1.53	0.87
0.530	1.551	0.87
*0.60	1.59	0.87
*0.70	1.56	0.88
0.759	1.494	0.89
*0.80	1.44	0.89
0.837	1.380	0.89
*0.90	1.23	0.91
0.930	1.148	0.92
0.972	0.817	0.94
—	—	—

(36) Logarithmic coördinates

Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$
0.10	$\bar{1}.215$	0.169
0.20	$\bar{1}.323$	1.925
0.30	$\bar{1}.394$	$\bar{1}.762$
0.40	$\bar{1}.453$	$\bar{1}.629$
0.50	$\bar{1}.514$	$\bar{1}.514$
0.60	$\bar{1}.577$	$\bar{1}.401$
0.70	$\bar{1}.652$	$\bar{1}.284$
0.80	$\bar{1}.745$	$\bar{1}.143$
0.90	$\bar{1}.864$	$\bar{2}.910$

TABLE V—(*Continued*)

(37) *o*-xylene alcohol

Water	Alcohol	Density
0.029	0.352	0.89
P. P. 0.04	0.53	—
*0.10	0.93	0.87
0.129	1.075	0.87
0.214	1.320	0.87
*0.30	1.53	0.87
0.312	1.560	0.86
*0.40	1.72	0.87
0.484	1.845	0.87
*0.50	1.87	0.87
*0.60	1.96	0.88
0.628	1.955	0.88
*0.70	1.94	0.88
0.792	1.813	0.89
*0.80	1.81	0.89
0.900	1.640	0.90
0.969	1.190	0.93

Tie-lines

Water	Water
0.00	0.64
0.00	0.21
0.00	0.16
0.00	0.13
0.00	0.11
0.02	0.88

(37) Logarithmic coördinates

Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$
0.10	$\bar{1}.032$	$\bar{1}.986$
0.20	$\bar{1}.180$	$\bar{1}.783$
0.30	$\bar{1}.292$	$\bar{1}.660$
0.40	$\bar{1}.367$	$\bar{1}.543$
0.50	$\bar{1}.427$	$\bar{1}.427$
0.60	$\bar{1}.486$	$\bar{1}.310$
0.70	$\bar{1}.557$	$\bar{1}.189$
0.80	$\bar{1}.645$	$\bar{1}.043$
0.90	$\bar{1}.739$	$\bar{2}.785$
P. P. —	$\bar{1}.878$	0.054

(38) *m*-xylene alcohol

Water	Alcohol	Density
0.033	0.388	0.88
0.098	0.800	0.87
*0.10	0.81	0.87
0.162	1.125	0.85
*0.20	1.30	0.85
0.289	1.590	0.85
*0.30	1.61	0.86
*0.40	1.77	0.86
0.408	1.775	0.86
*0.50	1.90	0.87
0.588	1.965	0.87
*0.60	1.98	0.87
*0.70	2.01	0.88
0.724	2.000	0.88
0.795	1.870	0.89
*0.80	1.87	0.89
0.898	1.530	0.90
*0.90	1.530	0.90
0.977	1.168	0.92

(38) Logarithmic coördinates

Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$
0.10	$\bar{1}.092$	0.046
0.20	$\bar{1}.187$	$\bar{1}.789$
0.30	$\bar{1}.271$	$\bar{1}.639$
0.40	$\bar{1}.354$	$\bar{1}.530$
0.50	$\bar{1}.420$	$\bar{1}.420$
0.60	$\bar{1}.482$	$\bar{1}.305$
0.70	$\bar{1}.542$	$\bar{1}.174$
0.80	$\bar{1}.631$	$\bar{1}.029$
0.90	$\bar{1}.770$	$\bar{2}.815$

TABLE V—(*Continued*)

(39) *p*-xylene alcohol (temp. 15°)

Water	Alcohol	Density
0.034	0.306	0.84
0.074	0.531	0.85
P. P. 0.08	0.57	—
*0.10	0.65	0.85
0.121	0.760	0.86
*0.20	1.05	0.85
0.211	1.092	0.85
0.286	1.310	0.85
*0.30	1.35	0.85
*0.40	1.56	0.85
*0.50	1.68	0.86
0.524	1.730	0.86
*0.60	1.77	0.86
0.622	1.783	0.86
0.702	1.743	0.87
0.807	1.625	0.88
*0.90	1.39	0.89
0.912	1.348	0.89
0.985	0.863	0.93

Tie-lines

Water	Water
0.00	0.26
0.01	0.19
0.02	0.16
0.04	0.14

(39) Logarithmic coördinates

Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$
0.10	$\bar{1}.187$	0.141
0.20	$\bar{1}.280$	$\bar{1}.881$
0.30	$\bar{1}.347$	$\bar{1}.715$
0.40	$\bar{1}.409$	$\bar{1}.585$
0.50	$\bar{1}.474$	$\bar{1}.474$
0.60	$\bar{1}.530$	$\bar{1}.354$
0.70	$\bar{1}.605$	$\bar{1}.237$
0.80	$\bar{1}.694$	$\bar{1}.092$
0.90	$\bar{1}.811$	$\bar{2}.857$
P. P. —	$\bar{1}.147$	0.208

(40) mesitylene alcohol

Water	Alcohol	Density
P. P. 0.03	0.48	—
0.037	0.516	0.86
0.090	0.981	0.86
*0.10	1.09	0.85
0.164	1.473	0.85
*0.20	1.66	0.84
0.298	2.030	0.85
*0.30	2.04	0.85
*0.40	2.32	0.85
0.429	2.365	0.85
*0.50	2.52	0.85
*0.60	2.64	0.86
*0.70	2.68	0.87
0.714	2.670	0.87
0.801	2.490	0.87
0.890	2.325	0.89
*0.90	2.28	0.89
0.949	1.615	0.90

Tie-lines

Water	Water
0.00	0.15
0.00	0.10
0.00	0.08

(40) Logarithmic coördinates

Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$
0.10	$\bar{2}.963$	$\bar{1}.917$
0.20	$\bar{1}.081$	$\bar{1}.683$
0.30	$\bar{1}.168$	$\bar{1}.536$
0.40	$\bar{1}.237$	$\bar{1}.413$
0.50	$\bar{1}.298$	$\bar{1}.298$
0.60	$\bar{1}.357$	$\bar{1}.181$
0.70	$\bar{1}.417$	$\bar{1}.049$
0.80	$\bar{1}.507$	$\bar{2}.905$
0.90	$\bar{1}.596$	$\bar{2}.642$
P. P. —	$\bar{2}.796$	0.306

TABLE V—(*Continued*)

(41) pinene alcohol

Water	Alcohol	Density
0.010	0.268	0.87
P. P. 0.015	0.47	—
0.055	1.001	0.85
0.103	1.595	0.85
0.205	2.268	0.84
*0.30	2.67	0.84
0.317	2.704	0.85
0.395	2.924	0.84
*0.40	2.94	0.85
0.507	3.135	0.85
0.607	3.126	0.86
0.707	3.038	0.86
0.806	2.799	0.87
0.906	2.331	0.89
0.965	1.639	0.91
—	—	—

(42) benzaldehyde alcohol

Water	Alcohol	Density
0.043	0.159	1.02
0.102	0.283	1.01
*0.20	0.42	0.99
0.211	0.441	0.99
0.295	0.520	0.98
*0.30	0.55	0.98
0.402	0.601	0.97
P. P. 0.43	0.61	—
0.504	0.643	0.96
0.606	0.681	0.95
0.702	0.701	0.95
*0.80	0.67	0.95
0.817	0.675	0.95
0.898	0.615	0.96
*0.90	0.61	0.96
0.969	0.461	0.97

Tie-lines

Water	Water
0.00	0.06
0.00	0.05
0.00	0.04
0.00	0.03
0.01	0.02

Tie-lines

Water	Water
0.04	0.98
0.09	0.96
0.10	0.82
0.15	0.76
0.26	0.63
0.31	0.57

(41) Logarithmic coördinates

Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$
0.10	$\bar{2}.799$	$\bar{1}.752$
0.20	$\bar{2}.945$	$\bar{1}.547$
0.30	$\bar{1}.051$	$\bar{1}.419$
0.40	$\bar{1}.134$	$\bar{1}.310$
0.50	$\bar{1}.203$	$\bar{1}.203$
0.60	$\bar{1}.283$	$\bar{1}.107$
0.70	$\bar{1}.362$	$\bar{2}.994$
0.80	$\bar{1}.456$	$\bar{2}.854$
0.90	$\bar{1}.587$	$\bar{2}.633$
P. P. —	$\bar{2}.504$	0.321

(42) Logarithmic coördinates

Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$
0.10	$\bar{1}.548$	0.502
0.20	$\bar{1}.648$	0.250
0.30	$\bar{1}.737$	0.105
0.40	$\bar{1}.823$	$\bar{1}.999$
0.50	$\bar{1}.893$	$\bar{1}.893$
0.60	$\bar{1}.946$	$\bar{1}.770$
0.70	$\bar{1}.999$	$\bar{1}.631$
0.80	0.077	$\bar{1}.475$
0.90	0.169	$\bar{1}.215$
P. P. —	$\bar{1}.848$	$\bar{1}.971$

TABLE V—(*Continued*)

(43) methyl aniline alcohol

Water	Alcohol	Density
0.041	0.218	0.96
*0.10	0.37	0.95
0.111	0.405	0.95
0.205	0.555	0.93
*0.30	0.68	0.93
0.331	0.721	0.93
P. P. 0.34	0.72	—
0.392	0.756	0.93
*0.40	0.76	0.93
0.498	0.835	0.93
*0.50	0.84	0.93
0.599	0.892	0.93
*0.60	0.89	0.93
0.697	0.901	0.93
*0.70	0.91	0.93
*0.80	0.87	0.94
0.813	0.856	0.94
0.902	0.734	0.95
0.959	0.581	0.96

Tie-lines

Water	Water
0.67	0.00
0.59	0.05
0.55	0.12
0.51	0.16
0.42	0.23

(43) Logarithmic coördinates

Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$
0.10	$\bar{1}.432$	0.386
0.20	$\bar{1}.561$	0.163
0.30	$\bar{1}.645$	0.013
0.40	$\bar{1}.721$	$\bar{1}.897$
0.50	$\bar{1}.775$	$\bar{1}.775$
0.60	$\bar{1}.829$	$\bar{1}.653$
0.70	$\bar{1}.886$	$\bar{1}.518$
0.80	$\bar{1}.964$	$\bar{1}.362$
0.90	0.091	$\bar{1}.137$
P. P. —	$\bar{1}.674$	$\bar{1}.962$

(44) *p*-nitrotoluene alcohol

Water	Alcohol	Density
0.022	0.253	1.08
P. P. 0.05	0.50	—
0.090	0.781	0.98
*0.10	0.84	0.97
*0.20	1.29	0.96
0.235	1.40	0.93
*0.30	1.57	0.92
0.337	1.649	0.92
*0.40	1.73	0.91
0.411	1.767	0.91
0.494	1.782	0.91
0.602	1.868	0.91
0.706	1.816	0.91
*0.80	1.63	0.91
0.809	1.607	0.91
0.898	1.395	0.92
*0.90	1.30	0.92
—	—	—
0.944	1.105	0.93

Tie-lines

Water	Water
0.00	0.14
0.02	0.10
0.03	0.08

(44) Logarithmic coördinates

Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$
0.10	$\bar{1}.076$	0.030
0.20	$\bar{1}.190$	$\bar{1}.793$
0.30	$\bar{1}.281$	$\bar{1}.649$
0.40	$\bar{1}.364$	$\bar{1}.540$
0.50	$\bar{1}.449$	$\bar{1}.449$
0.60	$\bar{1}.509$	$\bar{1}.333$
0.70	$\bar{1}.585$	$\bar{1}.217$
0.80	$\bar{1}.691$	$\bar{1}.089$
0.90	$\bar{1}.840$	$\bar{2}.886$
P. P. —	$\bar{1}.000$	0.279

TABLE V—(*Continued*)

(45) *o*-toluidine alcohol

Water	Alcohol	Density
0.046	0.025	1.01
*0.10	0.21	0.93
0.105	0.219	0.93
*0.20	0.32	0.97
0.222	0.346	0.97
0.298	0.404	0.96
*0.30	0.41	0.96
0.402	0.455	0.96
*0.50	0.48	0.96
0.546	0.492	0.95
0.580	0.493	0.95
*0.60	0.50	0.96
0.698	0.499	0.96
*0.70	0.50	0.96
*0.80	0.49	0.96
0.810	0.485	0.96
0.902	0.462	0.98
0.973	0.262	—

(46) isobutyl alcohol alcohol

Water	Alcohol	Density
*0.30	0.13	0.87
0.313	0.141	0.87
0.411	0.177	0.89
0.498	0.194	0.90
*0.50	0.20	0.90
*0.60	0.20	0.92
0.613	0.204	0.92
P. P. 0.65	0.21	—
0.696	0.205	0.94
*0.70	0.21	0.94
*0.80	0.20	0.95
0.868	0.189	0.96
—	—	—
—	—	—
—	—	—
—	—	—
—	—	—
—	—	—

Tie-lines

Water	Water
0.87	0.28
0.83	0.41
0.81	0.46
0.80	0.50

(45) Logarithmic coördinates

Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$
0.10	$\bar{1}.678$	0.632
0.20	$\bar{1}.796$	0.398
0.30	$\bar{1}.864$	0.232
0.40	$\bar{1}.944$	0.120
0.50	0.018	0.018
0.60	0.079	$\bar{1}.903$
0.70	0.146	$\bar{1}.778$
0.80	0.213	$\bar{1}.611$
0.90	0.291	$\bar{1}.337$

(46) Logarithmic coördinates

Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$
0.30	0.363	0.731
0.40	0.372	0.548
0.50	0.398	0.398
0.60	0.477	0.301
0.70	0.533	0.165
0.80	0.602	0.000
0.868	0.662	$\bar{1}.844$
P. P. —	0.491	0.222
—	—	—

TABLE V—(*Continued*)

(47) isoamyl alcohol alcohol

Water	Alcohol	Density
0.097	0.116	0.84
*0.10	0.12	0.84
0.203	0.258	0.85
0.306	0.396	0.86
0.398	0.427	0.88
0.503	0.449	0.89
0.601	0.453	0.90
0.706	0.434	0.92
P. P. 0.73	0.43	—
0.804	0.411	0.94
0.900	0.369	0.96
—	—	—
—	—	—
—	—	—
—	—	—
—	—	—
—	—	—
—	—	—
—	—	—

Tie-lines

Water	Water
0.95	0.10
0.94	0.31
0.92	0.40
0.87	0.53
0.83	0.63

(48) benzyl alcohol alcohol

Water	Alcohol	Density
*0.10	0.13	1.03
0.130	0.153	1.02
*0.20	0.26	1.00
0.209	0.268	1.00
0.295	0.347	0.98
*0.30	0.35	0.98
*0.40	0.39	0.98
0.422	0.392	0.98
*0.50	0.40	0.97
0.512	0.403	0.97
*0.60	0.41	0.97
P. P. 0.62	0.42	—
0.621	0.417	0.98
*0.70	0.41	0.97
0.712	0.404	0.97
0.806	0.388	0.97
0.898	0.352	0.97
*0.90	0.35	0.98
0.960	0.139	0.99

Tie-lines

Water	Water
0.33	0.92
0.41	0.83

(47) Logarithmic coördinates

Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$
0.10	$\bar{1}.921$	0.875
0.20	$\bar{1}.891$	0.493
0.30	$\bar{1}.921$	0.288
0.40	$\bar{1}.972$	0.148
0.50	0.047	0.047
0.60	0.122	$\bar{1}.946$
0.70	0.209	$\bar{1}.841$
0.80	0.290	$\bar{1}.688$
0.90	0.387	$\bar{1}.433$
P. P. —	0.230	$\bar{1}.798$

(48) Logarithmic coördinates

Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$
0.10	$\bar{1}.886$	0.840
0.20	$\bar{1}.880$	0.488
0.30	$\bar{1}.933$	0.301
0.40	0.011	0.187
0.50	0.097	0.097
0.60	0.165	$\bar{1}.989$
0.70	0.232	$\bar{1}.864$
0.80	0.312	$\bar{1}.710$
0.90	0.410	$\bar{1}.456$
P. P. —	0.169	$\bar{1}.957$

TABLE V—(*Continued*)

(49) phenetol alcohol (50) nitrobenzene alcohol (temp. 15°)

Water	Alcohol	Density	Water	Alcohol	Density
0.018	0.157	0.96	0.035	0.248	1.08
P. P. 0.10	0.55	—	P. P. 0.09	0.49	—
0.103	0.554	0.93	*0.10	0.53	1.02
0.202	0.916	0.90	0.109	0.558	1.02
0.293	1.170	0.90	*0.20	0.86	0.97
*0.30	1.18	0.90	0.214	0.901	0.97
0.394	1.380	0.89	*0.30	1.09	0.94
*0.40	1.39	0.89	0.316	1.112	0.94
0.505	1.518	0.89	0.406	1.238	0.93
0.601	1.560	0.89	0.494	1.300	0.92
0.694	1.545	0.90	*0.50	1.31	0.92
*0.70	1.54	0.90	*0.60	1.34	0.92
0.802	1.449	0.91	0.636	1.333	0.92
*0.90	1.21	0.92	0.694	1.305	0.91
0.918	1.156	0.93	*0.70	1.30	0.91
—	—	—	0.806	1.212	0.92
—	—	—	*0.90	0.98	0.93
—	—	—	0.909	0.940	0.93
—	—	—	0.980	0.601	0.95

Tie-lines

Water	Water
0.00	0.38
0.01	0.26
0.04	0.18
0.05	0.17
0.06	0.15

Tie-lines

Water	Water
0.00	0.42
0.00	0.33
0.01	0.24
0.03	0.16
0.05	0.14

(49) Logarithmic coördinates

Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$
0.10	$\bar{1}.260$	0.214
0.20	$\bar{1}.337$	$\bar{1}.939$
0.30	$\bar{1}.405$	$\bar{1}.773$
0.40	$\bar{1}.459$	$\bar{1}.636$
0.50	$\bar{1}.517$	$\bar{1}.517$
0.60	$\bar{1}.585$	$\bar{1}.409$
0.70	$\bar{1}.658$	$\bar{1}.290$
0.80	$\bar{1}.742$	$\bar{1}.140$
0.90	$\bar{1}.871$	$\bar{2}.917$
P. P. —	$\bar{1}.260$	$\bar{2}.214$

(50) Logarithmic coördinates

Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$
0.10	$\bar{1}.276$	0.230
0.20	$\bar{1}.367$	$\bar{1}.969$
0.30	$\bar{1}.440$	$\bar{1}.807$
0.40	$\bar{1}.512$	$\bar{1}.688$
0.50	$\bar{1}.582$	$\bar{1}.582$
0.60	$\bar{1}.651$	$\bar{1}.475$
0.70	$\bar{1}.731$	$\bar{1}.363$
0.80	$\bar{1}.820$	$\bar{1}.218$
0.90	$\bar{1}.963$	$\bar{1}.009$
P. P. —	$\bar{1}.264$	0.269

BIBLIOGRAPHY.

Author and reference.	Ternary system.
Schiff: Liebig's Ann., **118**, 370 (1861).	Water, alcohol, $MnSO_4$.
Tuchschmidt and Follenius: Ber. chim. Ges. Berlin, **4**, 583 (1871).	Water, alcohol, carb. bisulphide.
Berthelot and Jungfleisch: Ann. Chim. Phys., (4) **26**, 396 (1872).	Acetic acid, water, ether; bromine, water, carb. bisulphide.
Duclaux: Ann. Chim. Phys., (5) **7**, 264 (1876).	Benzene, water, acetic acid; amyl alcohol, water, alcohol; amyl alcohol, water, acetic acid; ether, water, acetic acid.
Draper: Chem. News, **35**, 87 (——).	Water, ether, hydroch. acid.
Traube and Neuberg: Zeit. Phys. Chem., **1**, 509 (1887).	Water, alcohol, ammon. sulph., etc
Wright and Collaborators: Proc. Roy. Soc., **45**, 461 (1889); **48**, 25 (1890); **49**, 156 and 174 (1891); **50**, 372 (1891); **52**, 11 (1892); **55**, 130 (1894).	Alloys.
Proc. Roy. Soc., **49**, 183 (1891).	Water, chloroform, acetic acid.
Bodländer: Zeit. phys. Chem., **7**, 318 (1891).	Water, alcohol, amm. sulph.
Pfeiffer: Zeit. phys. Chem., **9**, 469 (1892).	Water and alcohol with the following: mono-, di- and trichloracetic ester; amyl alcohol; methyl, ethyl, propyl, butyl and amyl formate; methyl, ethyl, propyl, butyl and amyl acetate; methyl, ethyl and propyl propionate; methyl, ethyl and propyl butyrate; methyl and ethyl valerate.
Schunke: Zeit. phys. Chem., **14**, 331 (1894)	Water, ether, hydrochl. acid.
Linebarger: Am. Chem. Jour., **14**, 380 (1892).	Water and alcohol with pot. carbonate, sod. carbonate, amm. sulphate, manganous sulphate; water and acetone with the same salts.
Krug and McElroy: Jour. Anal. Chem., **6**, 153 (1892).	Water and acetone with sugar, dextrose, maltose, sucrose.
Bancroft: Phys. Review, **3**, 21, 114 and 193 (1895); Jour. Phys. Chem., **1**, 34, and 760 (1896); **3**, 217 (1899).	Chloroform and water with alcohol, carbinol and acetone; benzene and water with alcohol, carbinol and ace-

Author and reference.	Ternary system.
	tone; ether and water with alcohol and carbinol; ethyl acetate and water with alcohol, carbinol and acetone; alcohol and water with the following: carbon bisulphid, methyl valerate, ethyl valerate, methyl butyrate, ethyl butyrate, amyl alcohol, mono-, di- and trichloracetic ester, ethyl isovalerate, isoamyl acetate, propyl butyrate, ethyl propionate, propyl propionate, propyl acetate, butyl acetate, amyl acetate, propyl formate, butyl formate, amyl formate.
Taylor: Jour. Phys. Chem., **1**, 301 (1896); Ibid., **1**, 461.	Water, benzene, alcohol (Binodal curve); water, benzene, alcohol (Tie-lines.
Schreinemakers: Zeit. phys. Chem., **22**, 93 and 515 (1897).	Theory.
23, 417 (1897).	Water, sod. chloride, succinonitrile (Tie-lines and binodal curve).
23, 649 (1897).	Water, ether, hydrochl. acid (exp. data of Draper and Schunke); water, alcohol, amm. sulphate (exp. data of Bodländer and Traube and Neuberg).
25, 543 (1898).	Water, ether, succinonitrile.
26, 237 (1898).	Water, benzoic acid, succinonitrile.
27, 95 (1898).	Water, alcohol, succinontrile.
29, 577 (1899).	Water, phenol, aniline.
30, 460 (1899).	Water, phenol, salt.
33, 74 (1900).	Water and phenol with tartaric and racemic acids.
33, 78 (1900).	Water, phenol, acetone.
39, 485 (1902).	Water, phenol, acetone (Tie-lines).
43, 305 (1903) (exps. by Middelberg).	Water, silver nitrate, succinonitrile.
Waddell: Jour. Phys. Chem., **2**, 233 (1898).	Benzene, water, acetic acid.
Snell: Jour. Phys. Chem., **2**, 457 (1898).	Pot. chloride, acetone, water; water, alcohol, mang. sulphate (exp. data of Schiff and Linebarger); water, alcohol, amm. sulphate (exp. data of Traube and Neuberg).
Lincoln: Jour. Phys. Chem., **4**, 161 (1900); Ibid., **8**, 248 (1904).	Water, benzene, alcohol; water, benzene, acetic acid.

Author and reference.	Ternary system.
Meerburg: Zeit. phys. Chem., **40**, 64 (1902).	Triethylamine and water with alcohol, ether, phenol.
Bell: Jour. Phys. Chem., **9**, 531 (1905).	Water, alcohol, pot. carb., etc. (exp. data of Linebarger); water, acetone, sugar, etc. (exp. data of Krug and McElroy); water, acetone, pot. carbonate; water, alcohol, pot. carbonate; water, acetic acid, sod. carbonate; water, acetic acid, sugar; water, acetic acid, naph.; water, acetic acid, anethol; water, alcohol, benzophenone; water, acetic acid, benzophenone.
Miller and McPherson: Jour. Phys. Chem., **12**, 709 (1908).	Water, chloroform, alcohol.

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University of Toronto,
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MATHEMATICAL THEORY OF THE CHANGES OF CONCENTRATION AT THE ELECTRODE, BROUGHT ABOUT BY DIFFUSION AND BY CHEMICAL REACTION

BY T. R. ROSEBRUGH AND W. LASH MILLER

Owing to the chemical changes which accompany electrolysis, the composition of the electrolyte at the electrodes is different from that in the body of the solution. Diffusion currents are consequently set up which tend to remove these differences; and if convection be avoided, the concentration of any constituent at any point in the solution will depend only on the initial composition of the solution, and on the amounts which have been carried to or from the electrodes by diffusion and by electrolytic migration.

In the simpler cases, at all events, these changes of concentration are susceptible of mathematical treatment; Weber[1] and Sand[2] have considered the case of electrolysis with constant currents, and Warburg[3] has deduced an equation for the stationary state on electrolysis with a sinusoidal current through a diffusion layer of "infinite" length. The present paper deals with the whole problem in a systematic manner, and includes the discussion of electrolysis with intermittent, successive and sinusoidal currents, without restriction as to the duration of the electrolysis or the length of the column of liquid through which the diffusion takes place. The increasing application of the oscillograph to the study of instantaneous conditions at the electrode led us to pay particular attention to the changes which occur within the first fraction of a second after throwing on the current, while Richards'[4] work on electrolysis with alternating currents,

[1] Wied Ann., 7, 536 (1879).
[2] Phil. Mag., [6] 1, 45 (1901); Zeit. phys. Chem., 35, 641 (1900).
[3] Wied. Ann., 67, 493 (1899).
[4] Trans. Am. Electrochem. Soc., 1, 221 (1902).

followed by the interesting experiments of LeBlanc[1] and of Reichinstein[2] with copper electrodes in cyanide solutions, induced us to include the case of non-instantaneous chemical reactions between the primary products of electrolysis and the other constituents of the solution.

The results of the investigation, however, are not perfectly general; for in leading up to Eqs. (*iii*) and (*xiv*) it has been assumed that both the diffusion constant and the flow due to electrolytic migration are independent of the concentration, and that the rate of the secondary reaction if any occur is proportional to the concentration of the constituent whose amount at the electrode is directly affected by the electrolysis—assumptions, which, in many cases, are not even approximately true. To treat the diffusion constant as a function of the concentration, or to consider reactions whose rates are proportional to any other than the first power of the concentration under consideration, would alter the whole nature of the differential equation involved; the restrictions thus imposed have been disregarded only in the comparatively simple, though important, case of prolonged electrolysis with a constant current.

To fix the ideas, electrolysis may be supposed to take place in a vessel of uniform cross section ($\mathscr{A}$ cm^2), bounded at the ends by the electrodes. The surface of each electrode is then identical in area and form with the cross section of the electrolyte, the current density will be uniform throughout, and the concentrations will be constant over each section of the solution taken parallel to the electrodes. The results of the argument are, however, equally applicable to the case of electrolysis with a rotating cylindrical electrode in a uniform field; in such cases, as shown by the experiments of Noyes and Whitney on rates of solution,[3] the electrode may be regarded as surrounded by an adherent layer of solution of uniform thickness through which diffusion takes place;[4]

[1] Zeit. phys. Chem., **46**, 213 (1903); Zeit. Elektrochemie, **11**, 705 (1905).
[2] Zeit. Elektrochemie, **15**, 734 (1909).
[3] Zeit. phys. Chem., **23**, 689 (1897).
[4] Ibid., **47**, 52 (1904).

with electrodes of ordinary dimensions this film has been found to be so thin[1] that the difference between the areas of its outer and inner surfaces may be neglected.

The direction normal to the surface of the electrodes is taken as the axis of x; it is assumed that at some fixed point on this axis the composition of the electrolyte (or at least the concentration z of the constituent under discussion) remains unaltered throughout the experiment, and this point is taken as the origin, $x = 0$, from which the values of x are reckoned. The "*solution condition*," then, adopted throughout this paper is that at $x = 0$, $z = z_0$ for all values of t, or

$$[For\ x = 0] \qquad \partial z/\partial t = 0 \qquad (i).$$

In Weber's experiments, where solutions of zinc sulphate were electrolyzed for long periods of time between stationary zinc electrodes, such a point of constant concentration evidently lies midway between the two electrodes; in experiments with a rotating electrode it will lie on the outer surface of the adherent liquid film, no matter how long the electrolysis proceeds if constituents removed at the cathode are replaced at the anode and vice versa, for some time at all events if the amount of electrolyte in the cell is large compared with that destroyed per minute by the electrolysis.

The position of one of the electrodes is defined by $x = l$; the other electrode is left out of consideration altogether, for as long as there is a section of the electrolyte where the concentration of one of the constituents remains unaltered, changes in the concentration of that constituent at one of the electrodes cannnot affect conditions at the other. It is true that some new substance, for instance acid formed at the anode, might on reaching the cathode affect the diffusion constants or the electrolytic migration of the others there; such cases, however, are excluded from consideration for other reasons (see pg. 820).

The distance in centimeters between the electrode under consideration and the section of fixed concentration is thus

[1] Zeit. phys. Chem., 47, 56 (1904).

denoted by l. Weber took the surface of one of his electrodes as origin and denoted the distance to the other by L; his L is thus twice l; with rotating electrodes, however, or stirred electrolytes, l is evidently quite independent of the distance between the electrodes.

At the moment of throwing on the current, the solution is supposed to be uniform throughout the vessel; thus the "*initial condition*" adopted in all the deductions of this paper is, that at $t = 0$, $z = z_0$ for all values of x or

$$[\textit{For } t = 0] \qquad \partial z/\partial x = 0 \qquad (ii).$$

When the current is thrown on, diffusion and migration begin.

Diffusion and Migration.—The rate of diffusion of any constituent away from one of the electrodes (*i. e.*, the number of equivalents of that substance per second which is carried by diffusion across each square centimeter of the cross section of the vessel) may be different at different points of the diffusion layer. At any point x, however, it is proportional to the concentration gradient at that point in the line connecting the electrodes; that is, to the difference of concentration per centimeter in the direction of the x axis, or

$$\textit{Rate of diffusion from electrode} = k\,\partial z/\partial x \quad - \quad - \quad - \quad (\textit{Fick}),$$

where z is the concentration of the constituent in question, expressed in equivalents per cubic centimeter; if $\partial z/\partial x$ be negative, diffusion will occur *towards* the electrode.

The rate of electrolytic migration of the same constituent, or the number of equivalents per second carried across each square centimeter of the cross section of the vessel by the current $\mathscr{I}$ amperes, is given by the expression

$$\textit{Rate of migration from electrode} = \frac{\mathscr{I}}{96540\,\mathscr{A}} \cdot \frac{zu}{\Sigma zu} \quad (\textit{Kohlrausch}),$$

where u is the mobility of the constituent in question and z its concentration; Σzu indicates the sum of the products of the mobilities of the various ions each into its own concentration. The sign of this expression (the direction in

which the migration takes place) evidently depends on the direction of the electric current, and on whether the constituent to which z refers acts as anion or cation; it is ***negative*** if the motion is *toward* the electrode.

Excluding for the present the possibility of secondary reactions in which the products of electrolysis take part, these two factors determine the total rate of flow, which accordingly is given by

$$\textit{Rate of flow from electrode} = k\frac{\partial z}{\partial x} + \frac{u}{96540\,\mathscr{A}}\cdot\frac{zu}{\Sigma zu},$$

and the rate of accumulation, $\partial z/\partial t$, at any point x is determined by the difference between the rates of flow to and from that point:

$$\frac{\partial z}{\partial t} = k\frac{\partial^2 z}{\partial x^2} + \frac{\partial}{\partial x}\left(\frac{\mathscr{I}}{96540\,\mathscr{A}}\cdot\frac{zu}{\Sigma zu}\right).$$

In some cases the second term on the right vanishes or may be neglected, leaving

$$\partial z/\partial t = k\partial^2 z/\partial x^2. \qquad (iii)$$

This occurs, for instance, (*a*) if $u = 0$, *i. e.*, if the constituent in question is a non-electrolyte; (*b*) if $zu/\Sigma zu$ is small, as when z refers to the concentration of copper in a solution of copper sulphate containing excess of sulphuric acid; (*c*) if the solution contains only one salt (in which case $zu/\Sigma zu$ becomes Hittorf's "transport number") whose transport number is not affected by change in concentration; (*d*) if the solution contains several salts with a common ion (the "constituent" under consideration) and if the ions of the opposite sign all have the same mobility; when the case is analogous to (*c*). Throughout Parts I and II of the present paper, (*iii*) is assumed to hold.

Electrode condition.—Let G represent the number of equivalents per second of the constituent under consideration caused to appear in the solution at each square centimeter of the surface of the electrode by the action of the current $\mathscr{I}$.

G will usually be related to $\mathscr{J}$ by an expression of the form

$$G = \frac{\mathscr{J}}{96540\,\mathscr{A}}\left(1 + \frac{zu}{\Sigma zu}\right)$$

in which the first term on the right measures the amount formed by chemical changes (oxidation, reduction, solution of the electrode, etc.), and the second term the amount brought up to (but, naturally, not past) the electrode surface by migration. At the anode in a solution of copper sulphate with excess of sulphuric acid, for instance, the first term would be positive and the second term zero if the "constituent under consideration"—to which z refers—were copper; if it were sulphuric acid, the first term would be zero and the second positive; in either case, if the electrode were a cathode, G would be negative.

The effect of the electrolysis on the concentration of this constituent in the solution is the same as though it were being carried into the solution through the surface of the electrode by the concentration gradient

$$[For\ x = l] \qquad \partial z/\partial x = G/k \qquad (iv)$$

which would produce the same gain that is actually brought about by the electrolysis. Eq. (*iv*) is therefore introduced as the "electrode condition" corresponding to the current $\mathscr{J}$ amperes. In the first Section of this paper, "Constant Current," G will be treated as independent of t; under "Successive Currents" it will be supposed to change abruptly at definite moments; while under "Sinusoidal Currents" it will be treated as a continuous function of the time. In the first Part of the paper it will be assumed that for a given value $\mathscr{J}$, of the current, G is not affected by the composition of the solution at the electrode; in the second Part, account will be taken of the fact that the nature of the chemical action at the electrode may change abruptly when the concentration reaches a certain value; Part III admits the possibility of secondary reactions at the electrode.

The mathematical problem then is, to find a solution for the differential equation (*iii*) which will satisfy the "boundary conditions" (*i*), (*ii*) and (*iv*). In the case of linear and homogeneous equations, like (*iii*), where the only coefficient k is a constant, there is no difficulty in finding particular solutions; from these, general solutions can be built up by multiplying each particular solution by an arbitrary constant and taking the sum. With such general solutions, however, in which the constants have arbitrary values, "ist so gut wie nichts gewonnen."[1] The main point is to find values for these multipliers such that the boundary conditions may be satisfied; and no general rules have as yet been laid down for finding them. Eq. (*iii*), however, has been made the subject of detailed study by Fourier and others in connection with the theory of the flow of heat,[2] and Weber[3] has shown how the boundary conditions of the present problem may be introduced; an equation corresponding to (15) of the present paper has already been obtained by him.

PART I

REACTIONS AT THE ELECTRODE INDEPENDENT OF THE CONCENTRATION z. SECONDARY REACTIONS EXCLUDED

Sec. 1.—Constant Current

One particular solution of (*iii*) is

$$z = Cx + D$$

and another is

$$z = (A \sin Ex + B \cos Ex)e^{-E^2kt} .$$

[1] Riemann, Die Partiellen Differential-Gleichungen der math. Physik, 4th Ed., Vol. i, pg. 153 (1900).

[2] In his "Introduction to the Theory of Fourier's Series and Integrals, and the Mathematical Theory of the Conduction of Heat" (Macmillan, 1906). H. S. Carslaw has collected a large number of cases in which problems analogous to the present have been solved, but as condition (iv) does not correspond to any easily realizable experimental condition except in the case of electrolysis, no problems satisfying that condition have been included; in the case of a heat problem, condition (iv) would correspond to a fixed rate of loss of heat from one end of a cylinder, independent of its temperature.

[3] Wied. Ann., 7, 536 (1879).

The expression built up from these, *viz.*,

$$z = (A_1 \sin E_1x + B_1 \cos E_1x)e^{-E_1^2kt} + (A_2 \sin E_2x + B_2 \cos E_2x)e^{-E_2^2kt} + \text{etc.} + Cx + D,$$

or briefly

$$z = \sum_{n=1}^{\infty} \{(A_n \sin E_nx + B_n \cos E_nx)e^{-E_n^2kt}\} + Cx + D, \quad (1)$$

proves sufficiently general to allow the introduction of (*i*), (*ii*) and (*iv*).

To introduce (*i*).—From (1)

$$[For\ x = 0] \qquad z = D + \Sigma B_n e^{-E_n^2kt}. \quad (2)$$

The expression on the right may be made constant and equal to z_0 for all values of t, as required by condition (*i*), by setting

$$B_1 = 0, \qquad B_2 = 0, \qquad B_3 = 0, \text{ etc.} \quad (3)$$

so that, from (2), (3) and (*i*)

$$D = z_0. \quad (4)$$

To introduce (*iv*).—From (1), (3) and (4),

$$[For\ x = l] \qquad \frac{\partial z}{\partial x} = C + \sum_{n=1}^{\infty} A_n e^{-E_n^2kt} . \cos E_n l \quad (5)$$

whence by (*iv*),

$$C + \sum_{n=1}^{\infty} A_n e^{-E_n^2kt} . \cos E_n l = \frac{G}{k}. \quad (6)$$

This is possible, for all values of t, only if each term involving t is separately made zero; this may be accomplished by setting

$$\cos E_n l = 0, \qquad i.\,e.,\ E_n = \frac{(2n-1)\pi}{2l}, \quad (7)$$

n being any integer.

From (6) and (7) there follows

$$C = G/k. \quad (8)$$

To introduce (*ii*).—Setting $t = 0$ in (1), and substituting

the values of B, D and E_n given by (3), (4) and (7), there follows

$$[For\ t = 0] \qquad z = z_0 + Cx + \sum_{n=1}^{\infty} A_n \sin \frac{(2n-1)\pi x}{2l}, \tag{9}$$

whence by (*i*)

$$0 = Cx + \sum_{n=1}^{\infty} A_n \sin \frac{(2n-1)\pi x}{2l}. \tag{10}$$

Fourier has shown that for values of f between 0 and $\pi/2$ (see Appendix)

$$f = \frac{4}{\pi}\left(\sin f - \frac{1}{9}\sin 3f + \frac{1}{25}\sin 5f - etc.\right), \tag{11}$$

whence (writing $\frac{\pi x}{2l}$ for f)

$$Cx = \frac{8lC}{\pi^2} \sum_{n=1}^{\infty} \frac{(-1)^{n+1}}{(2n-1)^2} \sin \frac{(2n-1)\pi x}{2l}. \tag{12}$$

Substituting this expression for Cx in (10)

$$\sum_{n=1}^{\infty} A_n \sin \frac{(2n-1)\pi x}{2l} = \frac{-8lc}{\pi^2} \sum_{n=1}^{\infty} \frac{(-1)^{n+1}}{(2n-1)^2} \sin \frac{(2n-1)\pi x}{2l} \tag{13}$$

whence

$$A_n = \frac{(-1)^n}{(2n-1)^2} \cdot \frac{8lc}{\pi^2}. \tag{14}$$

Thus, by substituting in (1) the values for B, D, E_n and A_n from (3), (4), (7) and (14), an expression is obtained,

$$z - z_0 = \frac{Gx}{k} + \frac{8lG}{\pi^2 k} \sum_{n=1}^{\infty} \frac{(-1)^n}{(2n-1)^2} \cdot e^{-\frac{(2n-1)^2\pi^2 kt}{4l^2}} \cdot \sin \frac{(2n-1)\pi x}{2l}, \tag{15a}$$

which satisfies the differential equation (*iii*) and the conditions (*i*), (*ii*) and (*iv*), if the current[1] remains constant from $t = 0$, the moment of throwing on the current, up to the moment t.

Inspection of (15*a*) shows that the right-hand member

[1] The equations deal only with G, which however is proportional to the current, see page 821.

is divisible by G. From this it appears that in experiments with the same electrolyte, carried out at the same temperature (hence with fixed value of k) and with the same rate of stirring (fixed value of l), the amount of change in concentration $(z-z_0)$ in a given time will be proportional to G and therefore to the current. It may also be concluded that if in a series of experiments (with fixed values of k and l) the currents (and therefore the values of G) be proportional to the initial concentrations (z_0), the values of z after any given duration of electrolysis (t) will likewise be proportional to the initial concentrations.

For the sake of brevity, (15*a*) may be written

$$z - z_0 = Cx + \frac{8lC}{\pi^2} \sum \frac{(-1)^n}{m^2} e^{-m^2at} \sin mgx, \qquad (15b)$$

where $m = 2n-1$, $C = G/k$, $a = \pi^2k/4l^2$, $g = \pi/2l$, and Σ is written for $\sum_{n=1}^{\infty}$. Since $(-1)^n \sin mgx = -\cos mg(l-x)$, (15*b*) may be put in the more convenient form,

$$\frac{z-z_0}{Cl} = \frac{x}{l} - \frac{8}{\pi^2} \sum \frac{1}{m^2} e^{-m^2at} \cos mg\xi, \qquad (15c)$$

where all the terms after the sign of summation are positive; ξ is here written as an abbreviation for $l-x$, the distance of the point x from the electrode. In this equation, the term on the left expresses the change in concentration as a fraction of the maximum change that could be brought about at the electrode by the same current;[1] the first term on the right gives the distance from the origin $(x = 0)$ as a fraction of the total length of the diffusion layer; and $at = \pi^2kt/4l^2$ in the exponent gives the time in units which depend on k and l only.[2]

The concentrations at the electrode, which are the most important from an experimental point of view, may be ob-

[1] *i. e.*, if left to act for "infinite" time, see p. 828, footnote. This "physical" interpretation of Cl is allowable within certain limits only (see Part II); the geometrical interpretation (fig. 1) holds in all cases.

[2] $a = \pi^2k/4l^2$ is spoken of later as the "time constant."

tained by substituting l for x in (15); $\cos mg\xi$ then becomes unity, and (15c) reduces to

$$[For\ x = l] \qquad \frac{z - z_0}{Cl} = 1 - \frac{8}{\pi^2} \sum \frac{1}{m^2} e^{-m^2 at}. \qquad (16)$$

Methods of Computation

First term approximation.—The first five terms of the series in (16) are:

$$e^{-at},\ \frac{1}{9} e^{-9at},\ \frac{1}{25} e^{-25at},\ \frac{1}{49} e^{-49at},\ \frac{1}{81} e^{-81at}.$$

The second term will be one percent or less of the first term if $\frac{1}{9} e^{-9at} = \frac{1}{100} e^{-at}$ or less, *i. e.*, if at be 0.301 or more; and it will be one per thousand of the first term if at be 0.589 or more; in both cases the remainder of the series is negligible. Thus in computing values of $(z - z_0)/Cl$ for values of at above 0.6, the first term of the series, neglecting all the others, will give results accurate to one-tenth percent; under these conditions (17) may therefore be used in place of (16).

$$[For\ \underline{at}\ large,\ and\ x = l] \quad \frac{z - z_0}{Cl} = 1 - \frac{8}{\pi^2} e^{-at} \quad approx. \quad (17)$$

But as at becomes smaller, the number of terms that have to be taken into account rises rapidly. In computing $(z - z_0)/Cl$ for $x = l$ and $at = 0.03$, for instance, the values of the first five terms (each multiplied by $8/\pi^2$) are 0.78664, 0.06875, 0.01532, 0.00378, 0.00088, respectively, and all five have to be evaluated in order to find $(z - z_0)/Cl$ to three places of decimals.

Parabolic approximation.—Thomson and Cayley[1] have shewn that

$$\sum_{n=1}^{\infty} e^{-\frac{(2n-1)^2\pi^2}{4f^2}} \cos \frac{(2n-1)\pi y}{f} =$$

$$\frac{f}{2\sqrt{\pi}} \left(e^{-y^2} - e^{-(y-f)^2} - e^{-(y+f)^2} + e^{-(y-2f)^2} + e^{-(y+2f)^2} - etc.\right). \quad (18)$$

[1] Quarterly Journal of Mathematics, 1, 316 (1857).

Substituting o for y, and at for $\pi^2/4f^2$, this gives

$$\sum_{n=1}^{\infty} e^{-(2n-1)^2 at} = \frac{1}{4}\sqrt{\frac{\pi}{at}}\left\{1 + 2\sum_{n=1}^{\infty}(-1)^n e^{-\frac{n^2\pi^2}{4at}}\right\}. \quad (19)$$

For small values of at the sum on the right may be neglected, giving

$$[\textit{For } \underline{at} \textit{ small}] \quad \sum_{n=1}^{\infty} e^{-(2n-1)^2 at} = \frac{1}{4}\sqrt{\frac{\pi}{a}} \quad \textit{approximately.} \quad (20)$$

Multiplying both sides by dt and integrating between the limits o and t there follows

$$[\textit{For } \underline{at} \textit{ small}] \quad \sum_{n=1}^{\infty} \frac{1}{m^2}\left(1 - e^{-(2n-1)^2 at}\right) = \frac{1}{2}\sqrt{\pi at} \textit{ approx.}, \quad (21)$$

whence

$$[\textit{For } x = l, \underline{at} \textit{ small}] \quad \frac{z - z_0}{Cl} =$$

$$1 - \frac{8}{\pi^2}\sum \frac{1}{m^2} e^{-m^2 at} = \frac{4}{\pi^{3/2}}\sqrt{at} \textit{ approx.}, \quad (22a)$$

or, substituting for at its value $\pi^2 kt/4l^2$,

$$[\textit{For } x = l \ \underline{at} \textit{ small}] \quad (z - z_0)/C = 1.129\sqrt{kt} \textit{ approximately.} \quad (22b)$$

TABLE I

Values of $(z - z_0)/Cl$ at the electrode

at	Parabolic approx.		True value (Eq. 16)	First term approx.	
	Calc. (Eq. 22a)	Error		Error	Calc. (Eq. 17)
0.4	0.45432	0.00012	0.45420	0.00246	0.45666
0.5	0.50795	0.00059	0.50736	0.00100	0.50836
0.6	0.55643	0.00169	0.55474	0.00041	0.55515

The figures of Table I show that for all practical purposes the accurate expression (16) may be replaced by the "first term approximation" (17) for values of at above 0.5, and by the "parabolic approximation" (22) for values of at below 0.5. It may not be out of place to emphasize the fact that the applicability of either of these approximations depends

not on the value of either l, k, or t alone, but on that of $at = \pi^2kt/4l^2$; the parabolic approximation, for instance, holds not only for the case "$l = \infty$",[1] as shown by Sand but it also holds for any other value of l provided kt be small enough.

TABLE II

Values of $(z - z_0)/Cl$ at the electrode

at	$(z - z_0)/Cl$	at	$(z - z_0)/Cl$	at	$(z - z_0)/Cl$
0	0	0.5	0.507	1.4	0.800
0.05	0.164	0.6	0.555	1.5	0.819
0.1	0.227	0.7	0.597	2.0	0.890
0.2	0.321	0.8	0.636	2.786	0.950
0.3	0.393	0.9	0.670	4.395	0.990
0.4	0.454	1.0	0.702	∞	1.000

As shown by the figures of Table II, ninety-nine percent of the total change of concentration at the electrode that a given current can accomplish is completed when at reaches 4.40. The actual number of seconds corresponding to a given value of at depends, obviously, on the "time constant" $a = \pi^2k/4l^2$, *i. e.*, on the values of k and l; if, for example, $k = 4 \times 10^{-6}$ cm^2/sec., and $l = 3.14 \times 10^{-4}$ cm (numbers within the range of those experimentally met with) at gives the duration of electrolysis in hundredths of a second; if the stirring were slower, however, and l rose to 3.14×10^{-3} cm, at would give the time in seconds.

The Stationary State

When the current has flowed long enough, the "stationary state" is reached, the equation for which may be obtained direct from (*iii*) by putting $\partial z/\partial t = 0$, or from (15) by setting $t = \infty$; the exponential term then becomes zero, and (15*c*) reduces to

$$[For\ t = \infty\ ^2]\quad z - z_0 = Cx \tag{23}$$

[1] Sand, Phil. Mag., [6] 1, 45 (1901).

[2] Practically speaking, for such values of at as make the sum term in (15) negligible. If one percent of $z - z_0$ be "negligible" from the point of view of the experimenter, $at = 4.40$ is high enough, so that for $k = 4 \times 10^{-6}$ and $l = 3.14 \times 10^{-4}$ cm, 0.044 second would be an "infinite" value of t.

i. e., there is a linear gradient of concentration throughout the diffusion layer.

The summation on the right of (15) thus shows the difference between the concentrations at any moment of the electrolysis and those at the stationary state; as with increasing t this term decreases, and ultimately vanishes, it will be spoken of as the "evanescent term" of (15) to distinguish it from the "stationary term" Cx.

The Stationary Term when k is a Function of z

Throughout this paper, the diffusion constant is supposed to be independent of the concentration; in the present paragraph, however, the important—but mathematically simple—case of the stationary state with constant current is dealt with on the assumption that k is a function of z. The equations deduced in this paragraph are not made use of in what follows.

Setting $k = f(z)$, the differential equation has the form:

$$\frac{\partial z}{\partial t} = \frac{\partial}{\partial x}\left(f(z)\frac{\partial z}{\partial x}\right). \tag{A}$$

As however at the stationary state, z depends on x alone, (A) may be replaced by the "ordinary" differential relation

$$\frac{d}{dx}\left(f(z)\frac{dz}{dx}\right) = 0. \tag{B}$$

Hence $f(z)\frac{dz}{dx}$ has a constant value for all values of x; at the electrode this is known to be equal to G; therefore,

$$f(z)\frac{dz}{dx} = G, \tag{C}$$

and

$$\int_{z_0}^{z} f(z)dz = \int_{0}^{x} Gdx = Gx; \tag{D}$$

therefore,

$$x = \frac{1}{G}\int_{z_0}^{z} f(z)dz, \tag{E}$$

which whenever $f(z)$ is known gives x explicitly in terms of z.

For example, if $f(z) = k_0 + k_1 z$ (F)

$$Gx = (k_0 z + \frac{1}{2} k_1 z^2) - (k_0 z_0 + \frac{1}{2} k_1 z_0^2). \quad \text{(G)}$$

From this, if desired, z may be expressed in terms of x, thus

$$z = \frac{-k_0 + \sqrt{k_0^2 + 2k_1(Gx + k_0 z_0 + \frac{1}{2} k_1 z_0^2)}}{k_1}. \quad \text{(H)}$$

Similarly in many other cases it is possible to pass from Eq. (E) to one expressing z in terms of x; when this is not possible, a graph may be drawn.

The "Limiting Current"

The "limiting current" for the change $z' - z_0$ is defined to be that current which at $t = \infty$ is just sufficient to bring the concentration at the electrode from z_0 to z'; it may be denoted by $\mathscr{I}'$ and the corresponding value of C by C'. Substituting z' for z, and l for x in (23),

[*For* $t = \infty$ *and* $x = l$] $z' - z_0 = C'l$,

$$\text{whence } C' = \frac{z - z_0}{l}, \text{ and } \mathscr{I}' = \frac{96540\, \mathscr{A} k(z' - z_0)}{l(1 + zu/\Sigma zu)}. \quad (24)$$

Thus any experiment in which z', z_0, and $\mathscr{I}'$ are measured may serve to determine the ratio k/l. In the special case where $z' = 0$, $\mathscr{I}'/z_0 = \frac{96540\, k\mathscr{A}}{(1 + zu/\Sigma zu)l}$. This relation has been used by Nernst and Merriam[1] and others for the determination of k/l.

As indicated by the heading of the table, the numbers entered in Table II give the values of $(z - z_0)/Cl$ at the electrode for different values of at. Since, however, from (24), $(z' - z_0)/Cl = C'/C = \mathscr{I}'/\mathscr{I}$, these same numbers give the limiting current $\mathscr{I}'$ corresponding to any arbitrary change of concentration at the electrode if the time (at) is known at which some known current $\mathscr{I}$ just brings about the same change. For example, the limiting current corresponding to

[1] Zeit. phys. Chem., 53, 235 (1905).

any change of concentration at the electrode is 0.164 times the current that will bring about the same change in the time $at = 0.05$. Conversely, the reciprocals of the numbers under $(z - z_0)/Cl$ give the current necessary to bring about any given change of concentration in a given time at, if the limiting current corresponding to the same change be known; to accomplish a given change in the time $at = 0.10$ requires 4.41 times the limiting current corresponding to that change. The "change of concentration" easiest recognized in the laboratory is often that from z_0 to 0.

Determination of k and of l

As both k and l are involved in (16), two experiments are in general required to determine both or either of them; one of these experiments may be a determination of the ratio k/l by means of the limiting current as indicated above, and the other a measurement in which the time needed to bring about some known change of concentration at the electrode is determined. If this second measurement be so planned that $at \geq 0.5$, the "single term" approximation (17) may be employed; writing η for the ratio k/l supposed known, this gives

$$l = \frac{0.4343\,\pi^2\eta t}{4\,log_{10}\left[\frac{\pi^2}{8}\left(1 - \frac{\eta(z' - z_0)}{G}\right)\right]} = \frac{1.072\,\eta t}{0.09121 + log_{10}\left(1 - \frac{\eta(z' - z_0)}{G}\right)}. \qquad (25)$$

If at be less than 0.5, however, so that the "parabolic approximation" (22*b*) is applicable, k may be determined by means of it directly from one experiment, the change of concentration at the electrode under those circumstances being independent of l. This method of finding k has been employed by Sand; in his experiments, however, l was taken to be "infinite," and was not determined.

Graphical Representation

The curves of Fig. 1 give the values of $(z - z_0)/Cl$ through

the diffusion layer (for any fixed values of C, k, and l), for $t = 0$, for $t = \infty$ and for ten values of at ranging from 0.1 to 1.0; the curves have been drawn with fair accuracy, values of $(z - z_0)/Cl$ may be estimated from them to within one

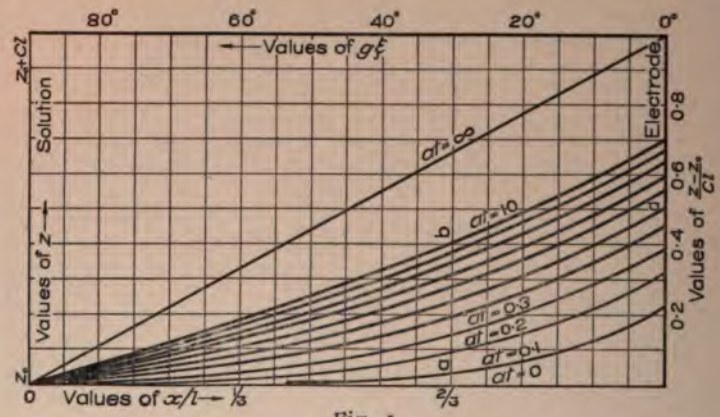


Fig. 1

percent of the value of Cl. As is clear from (15), values of z itself are not fixed by C, k, and l; the point $z = 0$ is therefore not marked on the diagram.

In Fig. 2, the same data are plotted on a time base;

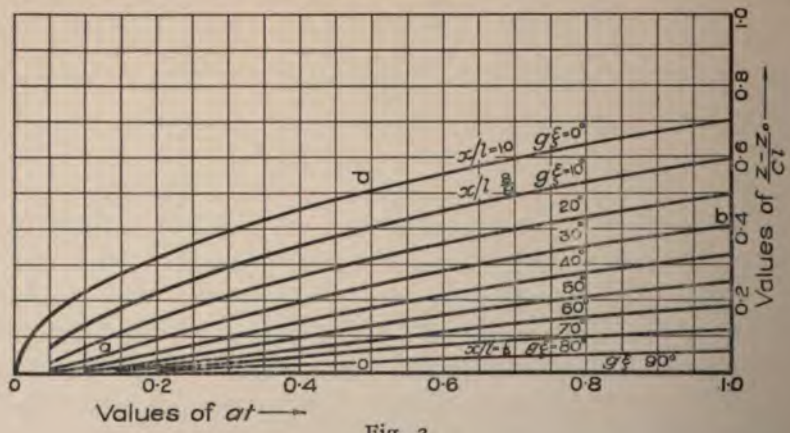


Fig. 2

the curves give the progress of the concentration change with the time (from $at = 0$, to $at = 1.0$) at ten equidistant cross-

sections of the diffusion layer. The line *ab* in Fig. 1 corresponds to the curve *ab* in Fig. 2, and the line *od* in Fig. 2 to the curve o*d* in Fig. 1.

In Fig. 3, the relative change of concentration at the electrode, $(z - z_0)/Cl$ is plotted for the interval $at = 0$ to $at = 5.0$; in Fig. 4 the same data are plotted with logarithmic coordinates

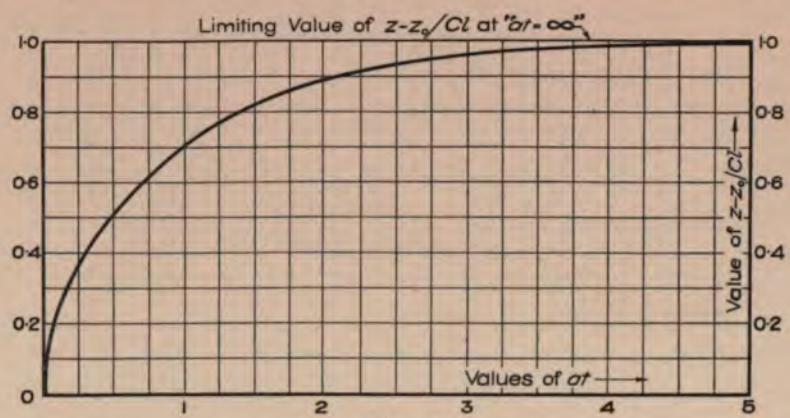


Fig. 3

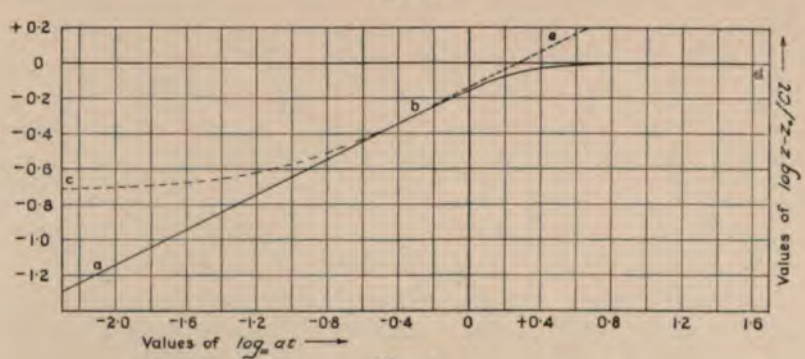


Fig. 4

(from $\log_{10} at = -2.30$ to 1.7, *i. e.*, from $at = 0.005$ to $at = 50$). The curve *dbc* represents the "first term approximation," the straight line *ea* the parabolic approximation, and the full line *abd* the true values of $\log_{10}(z - z_0)/Cl$.

Curve I of Fig. 5 gives the concentrations throughout he diffusion layer at $at = 0.5$ for fixed values of C and k

and for $l = l_1$; curve II gives the concentrations at $at = 0.1$ for the same values of C and k but for $l_2 = l_1\sqrt{5}$. Since a varies inversely as l^2, t as well as C and k is the same for both curves, and the figure serves to illustrate the conclusion of (22*b*) that for small values of at, $(z - z_0)/C$ at the electrode is independent of l. As shown by the figure, the change of

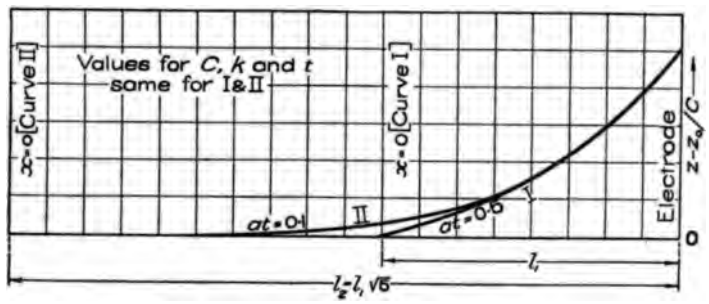


Fig. 5

concentration initiated at the electrode has hardly yet had time at $at = 0.1$ to spread more than half way to the "point of constant concentration," $x = 0$; shifting this point still further to the left could therefore have no effect on the concentration at the electrode.

Sec. 2.—Successive Currents in General

Eq. (15) and those deduced from it in the preceding paragraphs are applicable only when the current (and consequently C) remains constant during the electrolysis. It is now proposed to deal with the more general case where the currents $\mathscr{I}_1$, $\mathscr{I}_2$, $\mathscr{I}_3$, corresponding to C_1, C_2, C_3, etc., act successively, C_1 from $t = 0$ to $t = t_1$, C_2 from t_1 to t_2, C_3 from t_2 to t_3, etc; as before, at $t = 0$, $z = z_0$ for all values of x.

Up to the moment t_1, the values of z are given by (15); in particular,

$$[For\ t = t_1]\ z - z_0 = C_1x - \frac{8lC_1}{\pi^2}\sum\frac{1}{m^2}e^{-m^2at_1}\cos mg\xi \qquad (26a)$$

$$= C_2x + (C_1 - C_2)x - \frac{8lC_1}{\pi^2}\sum\frac{1}{m^2}e^{-m^2at_1}\cos mg\xi \qquad (26b)$$

$$= C_2x - \frac{8l}{\pi^2}\sum\frac{1}{m^2}(C_1e^{-m^2at_1} + C_2 - C_1)\cos mg\xi, \qquad (26c)$$

the last transformation being effected by means of (12), which, since $(-1)^{n+1} \sin mgx = \cos mg\xi$, may be brought into the form

$$Cx = \frac{8lC}{\pi^2} \sum \frac{1}{m^2} \cos mg\xi. \tag{27}$$

Between $t = t_1$ and $t = t_2$ values of z are given by the expression

$[For\ t_1 < t < t_2]\quad z - z_0 =$

$$C_2 x - \frac{8l}{\pi^2} \sum \frac{1}{m^2} \{C_1 e^{-m^2 a t_1} + \overline{C_2 - C_1}\} e^{-m^2 a(t - t_1)} \cos mg\xi \tag{28}$$

which satisfies *ii*, *iii*, *iv*,[1] and the condition that at $t = t_1$ the values of z along the x axis are those consequent on the action, from $t = 0$ to $t = t_1$, of the current $\mathcal{J}$.

In general

$[For\ t_{p-1} < t < t_p]\quad z - z_0 =$

$$C_p x - \frac{8l}{\pi^2} \sum \frac{1}{m^2} \Big\{ C_1 e^{-m^2 a t} + \overline{C_2 - C_1} e^{-m^2 a(t - t_1)} + \ldots\ldots$$

$$+ \overline{C_r - C_{r-1}} e^{-m^2 a(t - t_{r-1})} + \ldots + \overline{C_p - C_{p-1}} e^{-m^2 a(t - {}_{p-1})} \Big\} \cos mg\xi \tag{29a}$$

$$= C_p x - \frac{8}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{m^2} \Big\{ C_1 e^{-m^2 a t} + \sum_{r=2}^{p} \overline{C_r - C_{r-1}} e^{-m^2 a(t - t_{r-1})} \Big\} \cos mg\xi. \tag{29b}$$

The expression inside the brackets $\{\}$ can be rearranged thus:

$$\{C_1(e^{-m^2 a t} - e^{-m^2 a(t - t_1)}) + C_2(e^{-m^2 a(t - t_1)} - e^{-m^2 a(t - t_2)}) + \ldots.$$
$$+ C_r(e^{-m^2 a(t - t_{r-1})} - e^{-m^2 a(t - t_r)}) + \ldots. + C_p e^{-m^2 a(t - t_{p-1})}\}$$

so that (29) may also be written

$$[For\ t_{p-1} \leqq t \leqq t_p]\ z - z_0 = C_p x - \frac{8l}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{m^2} \Big\{ C_p e^{-m^2 a(t - t_{p-1})} +$$

$$\sum_{r=1}^{p-1} C_r(e^{-m^2 a(t - t_{r-1})} - e^{-m^2 a(t - t_r)}) \Big\} \cos mg\xi. \tag{29c}$$

---

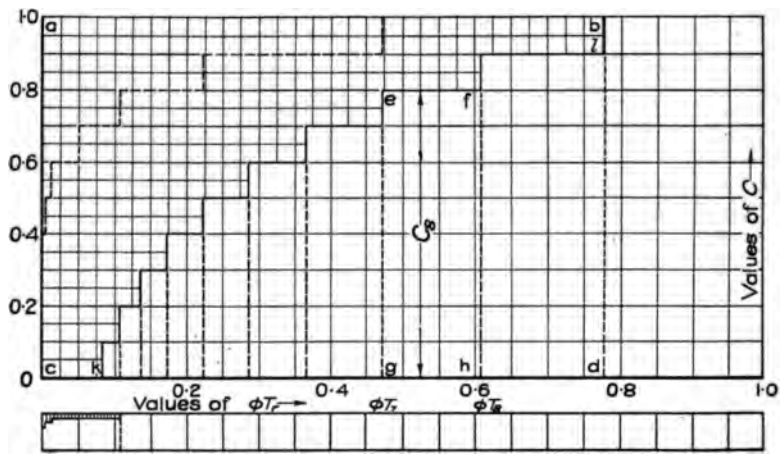
[1] This is obvious if it be noted that the expression within the brackets $\{\}$ is a function of m only, not of x or t.

Finally, if T_r be written for $t - t_r$, the time elapsed since the current corresponding to C_r ceased to act, and ϕT_r for $e^{-m^2a(t-t_r)}$,

$$[For\ t_{p-1} \leqq t < t_p] \quad z - z_0 \doteq C_p x - \frac{8l}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{m^2} \Big\} C_p \phi T_{p-1} - \sum_{r=1}^{p-1} C_r(\phi T_r - \phi T_{r-1}) \Big\} \cos mg\xi \quad (29d)$$

which lends itself to graphical representation.

Figs. 6 and 7 illustrate the case of electrolysis by a succession of currents beginning at $t = 0$ with one ampere, followed by 2, 3, 4, . . 10 amperes, each passing through the solution for the equal interval $at = 0.25$. The abscissae of the two



Figs. 6 and 7

figures give the values of ϕT_r for $n = 1$ and $n = 2$ respectively, and the ordinates the values of C and of $C/9$ respectively for the ten currents; thus Fig. 6 corresponds to the first term of the n-sum in (29*d*) and Fig. 7 to the second term. The area *abdc* equals $C_{10}\phi T_9$ (corresponding to $C_p\phi T_{p-1}$); *efhg* equals $(\phi T_8 - \phi T_7)C_8$, *kefld* equals $\sum_{r=1}^{p-1} C_r(\phi T_r - \phi T_{r-1})$, and *ackeflb* equals the whole expression within the { }

brackets of (29*d*), for $n = 1$. The broken line in the upper left-hand corner of Fig. 6 represents the first term of the n-sum for the same ten currents each persisting for $at = 0.75$ instead of $at = 0.25$; the great reduction of the $\{\ \}$ term of (29*d*) is obvious. It is quite clear from the figure, that the effect of previous history is much less on the second than on the first term, so that in deciding how far back it is necessary to go in taking account of the previous currents, the first term only need be considered.

Equation (29) in its various forms is the most general expression for $z - z_0$, all others given in Part I of this paper are deducible from it: Eq. (15) for instance results when $C_1 = C_2 = \ldots\ldots = C_p$; equations for the periodic recurrence of a finite number of currents are deduced from (29) in Secs. 3 and 4; and Sec. 5 shows how the periodic recurrence of an infinite number of currents each but slightly different from the preceding may be dealt with. As usual, by substituting l for x, whereupon $\cos mg\xi$ becomes unity, expressions for the experimentally important concentrations at the electrode may be obtained.

Sec. 3.—Periodic Currents. I. Cycles with Two Beats

In the first "beat" the current $\mathscr{J}_1$ acts for θ_1 seconds, in the second beat the current $\mathscr{J}_2$ for θ_2 seconds; these two "beats" make up a "cycle" of duration $\theta = \theta_1 + \theta_2$ seconds, which may be repeated again and again. It is convenient to introduce the symbol τ to represent the time elapsed since the beginning of the beat which is in progress at the moment t, t being counted as always from the moment $t = 0$ when the first current is thrown on; at $t = 0$, $z = z_0$ for all values of x.

In applying (29) to this case,

$$C_1 = C_3 = C_5, \textit{ etc.} \quad \theta_1 = t_1 = (t_3 - t_2) = (t_5 - t_4) = (t_7 - t_6), \textit{ etc.}$$
$$C_2 = C_4 = C_6, \textit{ etc.} \quad \theta_2 = (t_2 - t_1) = (t_4 - t_3) = (t_6 - t_5), \textit{ etc.}$$
$$\theta = t_2 = (t_4 - t_2) = (t_6 - t_4), \textit{ etc.} = \theta_1 + \theta_2.$$

Thus, during the pth beat, if p be odd ($p = 2q + 1$), $C_p = C_1$,

and $t = q\theta + \tau$; if p be even ($p = 2q$), $C_p = C_2$, and $t = (q - 1)\theta + \theta_1 + \tau$.

In the first case (p odd) on making these substitutions (29) becomes

$$[p\ odd]\quad z - z_0 = \tag{30a}$$
$$C_1x - \frac{8l}{\pi^2}\sum\frac{e^{-m^2at}}{m^2}\Big\{C_1 + (C_2 - C_1)[e^{m^2a\theta_1}(1 + e^{m^2a\theta} + e^{2m^2a\theta} + \ldots$$
$$+ e^{(q-1)m^2a\theta}) - e^{m^2a\theta}(1 + e^{m^2a\theta} + e^{2m^2a\theta} + \ldots + e^{(q-1)m^2a\theta})]\Big\}\cos mg\xi,$$

whence, summing the geometrical series, eliminating q, and rearranging,

$$[p\ odd]\ z - z_0 = C_1x + \frac{8l(C_2 - C_1)}{\pi^2}\sum\frac{e^{-m^2a\tau}}{m^2}\cdot\frac{e^{m^2a\theta} - e^{m^2a\theta_1}}{e^{m^2a\theta} - 1}\cos mg\xi$$
$$- \frac{8l}{\pi^2}\sum\frac{e^{-m^2at}}{m^2}\{C_1 + (C_2 - C_1)\frac{e^{m^2a\theta} - e^{m^2a\theta_1}}{e^{m^2a\theta} - 1}\}\cos mg\xi. \tag{30b}$$

Similarly, it may be shown that where p is even

$$[p\ even]\ z - z_0 = C_2x + \frac{8l(C_1 - C_2)}{\pi^2}\sum\frac{e^{-m^2a\tau}}{m^2}\cdot\frac{e^{m^2a\theta} - e^{m^2a\theta_2}}{e^{m^2a\theta} - 1}\cos mg\xi$$
$$- \frac{8l}{\pi^2}\sum\frac{e^{-m^2at}}{m^2}\{C_1 + (C_2 - C_1)\frac{e^{m^2a\theta} - e^{m^2a\theta_1}}{e^{m^2a\theta} - 1}\}\cos mg\xi. \tag{31}$$

In (30*b*) and (31), the term involving e^{-m^2at}, which decreases with increasing t and ultimately vanishes, may be spoken of as the "evanescent term"; it is the same in both equations, so that on plotting with z and t as axes the evanescent term would be represented by a continuous curve with no abrupt changes of direction at the beginning of a new beat. A plot of the "stationary terms" from the two equations (what is left of the right-hand members of (30*b*) and (31) when the evanescent term has been withdrawn) would give a zigzag line.

If x be replaced by l in these equations (and consequently $\cos mg\xi$ by unity) expressions for the concentrations at the electrodes are obtained. If t be set $= \infty$ thus reducing the evanescent term to zero, expressions for the concentrations at the stationary state are obtained. If τ be set $= 0$ (and consequently $e^{-m^2a\tau} =$ unity) expressions for the con-

centrations at the beginnings of odd or even beats (*i. e.*, at the ends of even or odd beats) respectively are obtained. If $C_2 = C_1$ the expression for constant current, (15), is obtained; if $C_2 = -C_1$ the equations apply to the simplest form of alternating current, and if $C_2 = 0$ to "intermittent" currents. Special cases of the latter will be examined in detail (see pages 840 and 843).

If the first, third, etc., beats last long enough to bring about a linear distribution of concentration throughout the diffusion layer, *i. e.*, if in (31), $a\theta_1 = \infty$ (see foot-note, page 828) the concentrations throughout the even beats will be represented by

$$[For\ \theta_1 = \infty]\ z - z_0 = C_2 x + \frac{8l(C_1 - C_2)}{\pi^2} \sum \frac{e^{-m^2 a\tau}}{m^2} \cos mg\xi. \quad (32)$$

Centre and Amplitude of Swing

When the stationary state is reached, *i. e.*, when the evanescent term has become zero or approximately so, the concentration at any point in the diffusion layer oscillates between two extreme values, one at the end of each beat. Half the sum of the extreme values of the concentration change gives the "centre of swing" or mean value of the concentration change at that point; half their difference gives the "amplitude" or greatest deviation of the concentration above and below its mean value. An expression for the amplitude, and one for $z - z_0$ at the centre of swing, may accordingly be obtained by taking half the difference and half the sum respectively of the values of $z - z_0$ given by (30*b*) and (31) after setting $t = \infty$ and $\tau = 0$.

$$[Amplitude]\ \frac{1}{2}(C_1 - C_2)x + \frac{4l(C_1 - C_2)}{\pi^2} \sum \frac{1}{m^2} \frac{e^{m^2 a\theta_1} + e^{m^2 a\theta_2} - 2e^{m^2 a\theta}}{e^{m^2 a\theta} - 1} \cos mg\xi. \quad (33)$$

$$[At\ centre]\ z - z_0 = \frac{1}{2}(C_1 + C_2)x + \frac{4l(C_1 - C_2)}{\pi^2} \sum \frac{1}{m^2} \frac{e^{m^2 a\theta_1} - e^{m^2 a\theta_2}}{e^{m^2 a\theta} - 1} \cos mg\xi. \quad (34)$$

Very Large and Very Small Values of θ

If both θ_1 and θ_2 are large, the concentration at any point oscillates between $z_0 + C_1x$ and $z_0 + C_2x$; on evaluating the θ fractions in (33) and (34), $\frac{1}{2}(C_1 + C_2)x$ is accordingly found as the expression for $z - z_0$ at the centre, and $\frac{1}{2}(C_1 - C_2)x$ for the amplitude.

When $a\theta$ is very small, the centre is $\left(C_1\frac{\theta_1}{\theta} + C_2\frac{\theta_2}{\theta}\right)x$ and the amplitude is very small; *i. e.*, the "zigzag" becomes almost a straight line. Thus the stationary state reached by electrolysis with a rapidly interrupted, alternated, or varied two-beat current is practically the same as would be reached by electrolysis with a constant current of the same number of coulombs per second (reckoned algebraically). Progress towards the stationary state is likewise the same in the two cases, as may be seen by evaluating the evanescent term of (30*b*) or (31) for very small values of θ_1 and θ_2. Stationary and evanescent terms together give:

[*For* θ *very small*] $z - z_0 =$

$$\left(C_1\frac{\theta_1}{\theta} + C_2\frac{\theta_2}{\theta}\right)x - \frac{8l}{\pi^2}\left(C_1\frac{\theta_1}{\theta} + C_2\frac{\theta_2}{\theta}\right)\sum\frac{e^{-m^2at}}{m^2}\cos mg\xi. \quad (35)$$

It may be noticed that this equation becomes equivalent to (15*c*) on writing $C_1\frac{\theta_1}{\theta} + C_2\frac{\theta_2}{\theta} = C$.

A Special Case of Intermittent Currents

To obtain an expression for the concentration changes at the electrode during electrolysis with an intermittent current, where the periods of electrolysis with the current C, and the intermissions, each last $0.5/a$ seconds, equations (30*b*) and (31) may be used setting $x = l$, $C_2 = 0$, $C_1 = C$, $a\theta_1 = a\theta_2 = 0.5$; so that $at = 0.5(p - 1) + a_\tau$, where a_τ changes from 0 to 0.5 during each beat.

The evanescent term (which of course is the same for both equations) and the two stationary terms are as follows:

$$\left.\begin{array}{ll}[\textit{Evanesc. term}] & -\dfrac{8lC}{\pi^2}\sum\dfrac{1}{m^2}\dfrac{e^{-m^2at}}{e^{0.5m^2}+1} \\ [\textit{Stat. term, } p \textit{ odd}] & Cl-\dfrac{8lC}{\pi^2}\sum\dfrac{1}{m^2}\dfrac{e^{m^2(0.5-ar)}}{e^{0.5m^2}+1} \\ [\textit{Stat. term, } p \textit{ even}] & \dfrac{8lC}{\pi^2}\sum\dfrac{1}{m^2}\dfrac{e^{m^2(0.5-ar)}}{e^{0.5m^2}+1}.\end{array}\right\} \quad (36)$$

Fig. 8 gives a graph of the evanescent term, and the stationary terms of (36) and their sum, *i. e.*, the values[1] of $(z - z_0)/Cl$ at the electrode.

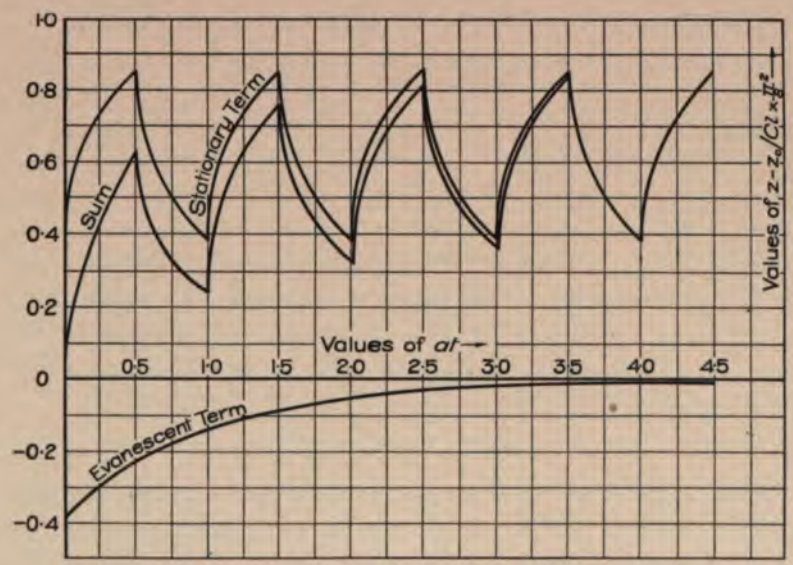


Fig. 8

Table III gives, for a number of values of $a\theta_1$ the values of $(z - z_0)/Cl$ at the electrode at the end of the 1st, 2d, 3d, 4th, and ∞th beats of current (*i. e.*, for $p = 1, 3, 5, 7,$ and ∞). The numbers under $p = 1$ are the same as those of Table II, those under $p = \infty$ are calculated from the stationary term of (31) after setting $x = l$, $\tau = 0$, $C_2 = 0$,

[1] The values actually plotted, however, are those here described multiplied by $\pi^2/_8 = 1.2337$.

$C_1 = C$; for purposes of computation this term is best put in the form:

$$[For\ p = \infty]\quad \frac{z - z_0}{Cl} = 1 - \frac{8}{\pi^2}\sum \frac{1}{m^2}\cdot\frac{1}{e^{m^2 a\theta_1} + 1}. \qquad (37)$$

The figures in a horizontal line of Table III thus give the ordinates of the peaks of $(z - z_0)$ - t - curves, such as "Sum" in Fig. 8 which corresponds to the line opposite $a\theta_1 = 0.5$. As the sum of the extreme values of $z - z_0$ at the electrode when $\theta_1 = \theta_2$ is $C_1 l$ (twice the "centre," Eq. 34), the difference between unity and the figure under $p = \infty$ gives the ordinates of the lowest points reached by the curve when the stationary state is attained.

Just as with Table II, however, the figures of Table III are susceptible of a second interpretation. Writing $\mathscr{I}''$ for the intermittent current (when $\theta_1 = \theta_2$) which just brings the concentration at the electrode from z_0 to the arbitrary value z' at the end of a beat of current, the figures of Table III obviously give $(z' - z_0)/C''l$ for various values of $a\theta_1$ and p. But by (24), $(z - z_0)/l = C'$, where C' corresponds the limiting current $\mathscr{I}'$, *i. e.*, to the constant current which at $t =$ can just reduce the initial concentration by the same amount. Therefore,

$$(z_0 - z')\,Cl = C'/C'' = \mathscr{I}'/\mathscr{I}'', \qquad (38)$$

and the reciprocals of the figures in Table III *give the intermittent currents* needed with different values of $\theta_1 = \theta_2$ to bring the concentration at the electrode to any arbitrary value at the end of the first, second, etc., beats of current, *as multiples of the limiting current* corresponding to the same change of concentration.

Thus, for example, if one ampere acting continuously is just sufficient to bring the concentration at the electrode from z_0 to any selected value z', the table shows that 1/0.507 amp. will be needed to bring about the same change in the time $a\theta_1 = 0.5$; while 1/0.625 amp. will do, if the current is allowed to pass for $a\theta_1 = 0.5$ and then again for the same period, after a pause of equal duration.

TABLE III

Values of $(z - z_0)/Cl$ at the electrode

Values of $a\theta_1 = a\theta_2$	$p = 1$	$p = 3$	$p = 5$	$p = 7$	$p = \infty$
2.00	0.890	0.903	0.903	0.903	0.903
1.50	0.819	0.851	0.852	0.852	0.852
1.00	0.703	0.771	0.781	0.782	0.782
0.50	0.507	0.625	0.668	0.684	0.693
0.10	0.227	0.299	0.353	0.395	0.586
0.05	0.160	0.212	0.250	0.281	0.561
0.01	0.072	0.095	0.112	0.126	0.527
0.005	0.049	0.067	0.079	0.089	0.519
0	0	0	0	0	0.500

The Simplest Alternating Currents

If C_1 and C_2 as defined by (*iv*) and (8) are of opposite signs, (30*b*) and (31) give the concentrations during electrolysis with the simplest form of alternating currents.

In the very simplest case, the two currents will be equal in strength, *i. e.*, $C_2 = -C_1$, and the beats will be of equal duration, *i. e.*, $\theta_1 = \theta_2$; on making these substitutions it will be found that (for both odd and even beats)

$$[For\ t = \infty\ and\ x = l] \quad \frac{z - z_0}{C_1 l} = 2\left[\frac{z - z_0}{Cl}\right] - 1 \qquad (39)$$

where the expression in square brackets denotes the corresponding values of $(z - z_0)/C_1 l$ (at $t = \infty$ and $x = l$) calculated for electrolysis with the simplest intermittent current, $C_2 = 0$, $\theta_1 = \theta_2$.

Thus by doubling the ordinates of the "stationary" curve in Fig. 8 and subtracting unity, points may be obtained for a graph of the concentrations at the stationary state when electrolyzing with the simplest alternating current, where $a\theta_1 = a\theta_2 = 0.5$. Similarly, ordinates for the peaks of the stationary curves for different values of $a\theta$ may be obtained by doubling the numbers under $p = \infty$ in Table III and subtracting unity.

In some cases it may be interesting to know the relation between C_1/C_2, θ_1, and θ_2 that will just bring $z - z_0$ to some

previously determined value at the end of a given beat of current. At the surface of a silver electrode in a solution of copper salt, it may be assumed, for the purpose of illustration, that when C is positive silver will go into solution, and that when C is negative silver (and not copper) will be redeposited so long as there is any left in the solution at the electrode. If there were no silver in the solution originally, part of that dissolved by the current (during the "anode beat." $C = C_1$) would diffuse away from the electrode; so in order to prevent the deposition of copper during the succeeding "cathode" beat ($C = C_2$, where C_2 as defined by (8) and (*iv*) is negative) either C_2 must be arithmetically less than C_1 or θ_2 must be less than θ_1.

Assuming that the two beats are of equal duration ($\theta_1 = \theta_2$), and that the stationary state has been reached, the concentration at the electrode at the end of a cathode beat will be represented by

$$\frac{z - z_0}{C_1 l} = 1 + \frac{8}{\pi^2}\left(\frac{C_2}{C_1} - 1\right)\sum \frac{1}{m^2}\,\frac{e^{m^2 a\theta_1}}{e^{m^2 a\theta_1} + 1}. \qquad (40)$$

Supposing $z_0 = 0$, *i. e.*, that there is (practically) no silver in the main body of the solution, the smallest value of C_1 that will prevent the deposition of copper during the cathode beats (where the current corresponds to C_2) may be calculated by setting $z = 0$ and solving for C_1/C_2.

The result is:

$$\frac{1}{1 - C_2/C_1} = \frac{8}{\pi^2}\sum \frac{1}{m^2}\,\frac{e^{m^2 a\theta_1}}{e^{m^2 a\theta_1} + 1}. \qquad (41a)$$

Values of the expression on the right have been tabulated (for another purpose) under $p = \infty$ in Table III; indicating them for the moment by N,

$$C_1/C_2 = -N/(1 - N). \qquad (41b)$$

The values in the following Table (IV) have been calculated by (41*b*). As an instance of their application, if $a\theta_1 = a\theta_2 = 0.5$, a current of 2.26 amperes while the silver was anode would be needed to prevent the deposition of copper by a current of one ampere in the opposite direction;

and a quantity of silver equal to that dissolved by the action of $\frac{1}{2}(2.26 - 1.00) = 0.63$ amperes acting for $\theta_1 + \theta_2 = 1.0/a$ seconds would pass through the diffusion layer into the outside solution during each cycle of $1.0/a$ seconds duration.

TABLE IV

$a\theta_1 = a\theta_2 =$	0	0.005	0.01	0.05	0.10	0.50	1.00	1.50	2.00
$-C_1/C_2 =$	1.00	1.08	1.11	1.28	1.42	2.26	3.59	5.76	9.31

Conversely, the concentration of the electrode solution at which black copper begins to be deposited during the electrolysis of copper sulphate solutions, and the effect of acid, etc., on that concentration, might be determined by measuring θ_1, θ_2, C_1, and C_2 in suitably planned experiments.

Sec. 4.—Periodic Currents. II. Cycles with Four Beats.

One case only need be considered in detail. If the two currents referred to in the discussion of cycles with two beats be obtained from a commutator made of copper bars separated by some insulating material, (30*b*) and (31) are not strictly applicable; for in reality the cycle will consist of four beats, the first lasting θ_1 seconds with a current corresponding to C_1, the second for the short period d seconds during which the brush is passing the insulation and no current flows, the third for θ_2 seconds with current corresponding to C_2, and finally the fourth with no current for d seconds again. The duration of the cycle may be represented by $\theta = \theta_1 + \theta_2 + 2d$.

By inserting the proper values in (29*c*) the following expressions may be obtained:

$$[For\ p = 4q + 1]\quad z - z_0 = C_1 x - \frac{8l}{\pi^2}\sum \frac{e^{-m^2 a\tau}}{m^2}\,(C_1 + B_m \cos mg\xi) + \frac{8l}{\pi^2}\sum \frac{e^{-m^2 at}}{m^2}\,B_m \cos mg\xi \qquad (42)$$

$$[For\ p = 4q + 3]\quad z - z_0 = C_2 x - \frac{8l}{\pi^2}\sum \frac{e^{-m^2 a\tau}}{m^2}\left[C_2 + C_1\left\{e^{-m^2 a(\theta_1 + d)} - e^{-m^2 ad}\right\} + B_m e^{-m^2 a(\theta_1 + d)}\right] \cos mg\xi + \frac{8l}{\pi^2}\sum \frac{e^{-m^2 at}}{m^2} B_m \cos mg\xi. \qquad (42)$$

where

$$B_m(e^{m^2a\theta} - 1) = C_1(1 - e^{m^2a\theta_1}) + C_2\{e^{m^2a(\theta_1 + d)} - e^{m^2a(\theta_1 + \theta_2 + d)}\}.$$

If $d = 0$, the two equations (42) reduce to (30*b*) and (31) respectively. It may be noticed that their evanescent terms are identical.

Sec. 5.—Periodic Currents. III. Sinusoidal Currents, Fourier Form.

If the difference between any two successive currents be infinitely small, and the number of currents be infinite, the difference $C_r - C_{r-1}$ in (29*b*) becomes a differential, and the summation with respect to r becomes an integration. Values for the concentration-changes during electrolysis with a sinusoidal current, where

$$[At \text{ and after } t = 0] \quad C = M \sin(\omega t + \alpha)$$

may thus be obtained.

Writing u in place of t_r to save printing, (29*b*) becomes:

$$z - z_0 = Mx \sin(\omega t + \alpha) - \frac{8l}{\pi^2}\sum\frac{1}{m^2}\Big\{Me^{-m^2at}\sin\alpha + \int_0^t M\omega e^{-m^2a(t-u)}\cos(\omega u + \alpha)du\Big\}\cos mg\xi, \quad (43a)$$

$$= Mx\sin(\omega t + \alpha) - \frac{8l}{\pi^2}\sum\frac{1}{m^2}\Big\{Me^{-m^2at}\sin\alpha + \frac{M\omega e^{-m^2at}}{m^4a^2 + \omega^2}[e^{m^2at}(\omega\sin\overline{\omega t + \alpha} + m^2a\cos\overline{\omega t + \alpha}) - (\omega\sin\alpha + m^2a\cos\alpha)]\Big\}\cos mg\xi. \quad (43b)$$

$$= Mx\sin(\omega t + \alpha) - \frac{8lM\omega}{\pi^2}\sum\frac{1}{m^2}\frac{\omega\sin\overline{\omega t + \alpha} + m^2a\cos\overline{\omega t + \alpha}}{m^4a^2 + \omega^2}\cos mg\xi - \frac{8lMa}{\pi^2}\sum\frac{m^2a\sin\alpha - \omega\cos\alpha}{m^4a^2 + \omega^2}e^{-m^2at}\cos mg\xi. \quad (43c)$$

$$= \frac{2Mk}{l}\sum\frac{m^2a\sin\overline{\omega t + \alpha} - \omega\cos\overline{\omega t + \alpha}}{m^4a^2 + \omega^2}\cos mg\xi - \frac{2Mk}{l}\sum\frac{m^2a\sin\alpha - \omega\cos\alpha}{m^4a^2 + \omega^2}e^{-m^2at}\cos mg\xi. \quad (43d)$$

(43*d*) being derived from (43*c*) by using (27) and writing $\pi^2k/4l^2$ for a in the coefficient of the summation.

The last term on the right of (43*c*) and (43*d*) constitutes the "evanescent term", while the first term and the first sum together in (43*c*) or the first sum in (43*d*) form the "stationary term" which alone remains when the stationary state is reached. If $\omega = 0$, (43) reduces to (15) with $M \sin\alpha$ in place of C.

The same method may obviously be employed for expressing the concentration changes produced by currents which vary with the time according to any other law. Writing $C = f(t)$, (29) becomes

$$z - z_0 = xf(t) - \frac{2k}{l}\sum\left\{\frac{f(t)}{m^2a} - e^{-m^2at}\int_0^t e^{m^2au}f(u)\,du\right\}\cos mg\xi. \quad (44a)$$

$$= \frac{2k}{l}\sum\left\{e^{-m^2at}\int_0^t e^{m^2au}f(u)\,du\right\}\cos mg\xi. \quad (44b)$$

The Stationary State When $l\sqrt{\frac{\omega}{k}}$ is Large

The exponential multiplier, e^{-m^2at}, causes the series in the evanescent term to converge more rapidly than that in the stationary term; with large values of l particularly, the convergence of the latter is very slow. In the next section another form of the stationary term will be obtained which is more suitable for computation; here it is proposed to find the special value assumed by the stationary term of (43*d*) when $l\sqrt{\frac{\omega}{k}} = \infty$.

The stationary term may be written

$$\sum_{n=1}^{\infty}\frac{2m^2akM\sin\overline{\omega t + \alpha}}{m^4a^2 + \omega^2}\cos mg\xi$$

$$-\sum_{n=1}^{\infty}\frac{2kM\omega\cos\overline{\omega t + \alpha}}{m^4a^2 + \omega^2}\cos mg\xi. \quad (45a)$$

Defining[1] $H = \xi\sqrt{\frac{\omega}{k}}$, $\mu = \sqrt{\frac{\omega}{2k}}$, and $\psi = m\sqrt{\frac{a}{\omega}} = \frac{(2n-1)\pi}{2l}\sqrt{\frac{k}{\omega}}$; while n increases by unity, ψ increases by $\Delta\psi = \frac{\pi}{l}\sqrt{\frac{k}{\omega}}$.

Introducing these symbols (45*a*) becomes

$$\frac{\sqrt{2}.M\sin\overline{\omega t+\alpha}}{\pi\mu}\sum_{n=1}^{\infty}\frac{\psi^2\cos H\psi}{\psi^4+1}\Delta\psi$$

$$-\frac{\sqrt{2}.M\cos\overline{\omega t+\alpha}}{\pi\mu}\sum_{n=1}^{\infty}\frac{\cos H\psi}{\psi^4+1}\Delta\psi. \qquad (45b)$$

As $l\sqrt{\frac{\omega}{k}}$ increases, ψ decreases; until when $l\sqrt{\frac{\omega}{k}} = \infty$, $\Delta\psi = d\psi$ and the summation from $n = 1$ $\left(\text{or } \psi = \frac{\pi}{2l}\sqrt{\frac{k}{\omega}}\right)$ to $n = \infty$ becomes an integration between the limits 0 and ∞.

$$[\textit{For } l\sqrt{\frac{\omega}{k}} = \infty\,]\ \textit{Stat. term} = \frac{\sqrt{2}M\sin\overline{\omega t+\alpha}}{\pi\mu}\int_0^{\infty}\frac{\psi^2\cos H\psi}{\psi^4+1}d\psi$$

$$-\frac{\sqrt{2}\,M\cos\overline{\omega t+\alpha}}{\pi\mu}\int_0^{\infty}\frac{\cos H\psi}{\psi^4+1}d\psi. \qquad (46a)$$

By using the partial fractions $\frac{2\psi^2}{1+\psi^4} = \frac{i}{1+\psi^2 i} - \frac{i}{1-\psi^2 i}$, and $\frac{2}{1+\psi^4} = \frac{1}{1+\psi^2 i} + \frac{1}{1-\psi^2 i}$, where $i = \sqrt{-1}$, and setting ϕ^2 alternately equal to $\psi^2 i$ and to $-\psi^2 i$ these integrals may be made to depend upon the known form

$$\int_0^{\infty}\frac{\cos n\phi}{\phi^2+1}d\phi = \frac{\pi}{2}e^{-n}.$$

Their values are:

$$\left.\begin{aligned}\int_0^{\infty}\frac{\psi^2\cos H\psi}{\psi^4+1}d\psi &= -\frac{\pi}{2}e^{-\frac{H}{\sqrt{2}}}\sin\left(\frac{H}{\sqrt{2}}-\frac{\pi}{4}\right)\\ \int_0^{\infty}\frac{\cos H\psi}{\psi^4+1}d\psi &= \frac{\pi}{2}e^{-\frac{H}{\sqrt{2}}}\sin\left(\frac{H}{\sqrt{2}}+\frac{\pi}{4}\right).\end{aligned}\right\} \qquad (47)$$

[1] This use of the letters H, ϕ and ψ, is restricted to equations (45) and (46).

Introducing these values in (46*a*) and rearranging

$$[For\ l\sqrt{\frac{\omega}{k}} = \infty]\ Stat.\ term = \frac{-M}{\mu\sqrt{2}}\, e^{-\mu\xi} \cos\left(\omega t + \alpha - \mu\xi + \frac{\pi}{4}\right) \quad (46b)$$

$$= \frac{M}{\mu\sqrt{2}}\, e^{-\mu\xi} \sin\left(\omega t + \alpha - \mu\xi - \frac{\pi}{4}\right). \quad (46c)$$

This expression has already been obtained by Warburg,[1] for "$l = \infty$,"[2] direct from the differential equation, by means of a Fourier's integral.

Sec. 6.—Sinusoidal Currents Continued (Hyperbolic Form)

The expression (43) for the concentrations throughout the diffusion layer during electrolysis with a sinusoidal current, which has been deduced in the preceding section, is in many cases very inconvenient for purposes of computation. In the present section another form will be obtained; for this purpose, however, it is necessary to go back to the original differential equation.

In (1), *viz.*:

$$z - D = Cx + \Sigma(A_n \sin E_n x + B_n \cos E_n x)e^{-E_n^2 kt} \quad (1)$$

the "stationary term" (S) is Cx, it fulfils the conditions

[*Solution condition*] *At* $x = 0$, $\partial S/\partial t = 0$ *for all values of* t (*v*)
[*Electrode condition*] *At* $x = l$, $\partial S/\partial x = C$ *for all values of* t (*vi*)

while the "evanescent term" (V), *viz.* the summation, is made to fulfil the conditions

[*Solution condition*] *At* $x = 0$, $\partial V/\partial t = 0$ *for all values of* t (*vii*)
[*Electrode condition*] *At* $x = l$, $\partial V/\partial x = 0$ *for all values of* t (*viii*)
[*Initial condition*] *At* $t = 0$, $V + S = 0$ *for all values of* x (*ix*)

by assigning suitable values to A_n B_n and E_n. Each term separately is a particular solution of the differential equation (*iii*).

By the use of Fourier's series, as illustrated on pg. 824, it is obviously possible to make the evanescent term comply

[1] Wied. Ann., 67, 493 (1899).
[2] See page 854.

with the three conditions *vii*, *viii*, and *ix*, no matter what S may be; so that if it were possible to construct a stationary term which was a solution of (*iii*) and for which in addition

[*Solution condition*] *At* $x = 0$, $\partial S/\partial t = 0$ *for all values of* t (*v*)

[*Electrode condition*] *At* $x = l$, $\partial S/\partial x =$
$M \sin(\omega t + \alpha)$ *for all values of* t, (*x*)

an expression could be obtained directly for the values assumed by z during electrolysis with the current $\mathscr{I} = \dfrac{96540\,\mathscr{A} M k \sin(\omega t + \alpha)}{1 + zu/\Sigma zu}$ amperes (see pg. 821).

This course is followed in the succeeding paragraphs. and the resulting equation (59), while identical in meaning with (43), is much more convenient in form for certain computations.

(*a*) *The Stationary Term, S*

A hint as to the general form with which to begin is furnished by the exponential form of the evanescent term in (1).

Let $$S = (A_1 e^{\gamma x} + A_2 e^{-\gamma x}) e^{\gamma^2 kt} + (B_1 e^{\lambda x} + B_2 e^{-\lambda x}) e^{\lambda^2 kt}. \qquad (48)$$

By differentiating it will be seen at once that to satisfy (*v*) it is necessary to set

$$A_2 = -A_1, \quad \text{and} \quad B_2 = -B_1. \qquad (49)$$

Because of (*x*) — writing A for A_1, and B for B_1, and putting $M \sin(\omega t + \alpha)$ in the exponential form[1] —

$$\gamma A(e^{\gamma l} + e^{-\gamma l}) e^{\gamma^2 kt} + \lambda B(e^{\lambda l} + e^{-\lambda l}) e^{\lambda^2 kt} = \frac{M}{2i}(e^{i(\omega t + \alpha)} - e^{-i(\omega t + \alpha)}) \qquad (50)$$

[1] The relations used in making the transformations of these paragraphs are:

$i = \sqrt{-1}$

$2 \cos y = e^{iy} + e^{-iy}$ $\qquad$ $2i \sin y = e^{iy} - e^{-iy}$

$2 \cosh y = e^{y} + e^{-y}$ $\qquad$ $2 \sinh y = e^{y} - e^{-y}$

$\sinh 2y = 2 \sinh y \,.\, \cosh y$

$\cosh 2y = \cosh^2 y + \sinh^2 y$

$\cosh^2 y - \sinh^2 y = 1$

$\sqrt{i} = (1 + i)/\sqrt{2}$ $\qquad$ $\log \text{nat}\, i = (-1)^{n+1}(2n - 1)i\pi/2$

$\sqrt{-i} = (1 - i)/\sqrt{2}$

which can be satisfied by setting

$$\gamma^2 k = i\omega, \quad \textit{whence } \gamma = (1 + i)\sqrt{\frac{\omega}{2k}} \tag{51}$$

$$\lambda^2 k = -i\omega, \textit{ whence } \lambda = (1 - i)\sqrt{\frac{\omega}{2k}}, \tag{52}$$

$$A = \frac{Me^{i\alpha}}{2i\gamma(e^{\gamma l} + e^{-\gamma l})}, \quad B = \frac{-Me^{-i\alpha}}{2i\lambda(e^{\lambda l} + e^{-\lambda l})}. \tag{53}$$

Introducing these values of A, B, γ, l into (48), (*iii*) (*v*) and (*x*) are satisfied, and the result may be written

$$S = \frac{M}{2\mu}\{(J - H)(F\cos - G\sin) + (J + H)(F\sin + G\cos)\} \tag{54a}$$

$$= \frac{-M}{2\mu}\{(JG - HF)(\sin - \cos) - (HG + JF)(\sin + \cos)\}, \tag{54b}$$

$$= \frac{-M}{\mu\sqrt{2}}\{(JG - HF)\cos\overline{\omega t + \alpha - \tfrac{3}{4}\pi} + (HG + JF)\sin\overline{\omega t + \alpha - \tfrac{3}{4}\pi}\} \tag{54c}$$

$$= \frac{M}{\mu\sqrt{2}}\sqrt{(F^2 + G^2)(H^2 + J^2)}\,.\,\sin(\omega t + \alpha + \gamma - \tfrac{1}{4}\pi), \tag{54d}$$

where

$$\mu = \sqrt{\frac{\omega}{2k}},$$

$$F = \cosh l\mu \ \cos l\mu/(\cos^2 l\mu + \sinh^2 l\mu),$$

$$G = -\sinh l\mu\,.\,\sin l\mu/(\cos^2 l\mu + \sinh^2 l\mu),$$

$$H = \sinh \mu x\,.\,\cos \mu x,$$

$$J = \cosh \mu x\,.\,\sin \mu x,$$

$$\gamma = \tan^{-1}(JF + HG)/(HF - JG),$$

"*sin*" and "*cos*" are written, in (54*a*) and (54*b*) only, for *sin* $(\omega t + \alpha)$ and *cos* $(\omega t + \alpha)$ respectively.

Conversion of the Hyperbolic Form of S into the Fourier Form

To check this result, (54) may be converted into the stationary term of (43); the form (54*a*) is the most convenient for the transformation. It is first neces-

sary to develop J and H as series of sines of odd multiples of $\pi x/2l$

Writing $m = 2n - 1$, $P = 2l\mu/\pi$, $\Theta = \pi x/2l$, the series are:

$$J = \cosh \mu x \,.\, \sin \mu x = \cosh P\Theta \,.\, \sin P\Theta =$$

$$4P(-1)^{\frac{m-1}{2}} \sum \frac{(m^2 + 2P^2)\cosh l\mu \,.\, \cos l\mu - (m^2 - 2P^2)\sinh l\mu \,.\, \sin l\mu}{m^4 + 4P^4} \sin m\Theta.$$

$$H = \sinh \mu x \,.\, \cos \mu x = \sinh P\Theta \,.\, \cos P\Theta =$$

$$4P(-1)^{\frac{m-1}{2}} \sum \frac{(m^2 + 2P^2)\cosh l\mu \,.\, \cos l\mu - (m^2 - 2P^2)\sinh l\mu \,.\, \sin l\mu}{m^4 + 4P^4} \sin m\Theta.$$

On carrying out the multiplications and additions indicated in (54*a*), writing g for $\pi/2l$, and replacing $(-1)^{\frac{m-1}{2}} \sin m\Theta$ by $\cos mg\xi$, the expression for S becomes

$$S = \frac{2Mk}{l} \sum \frac{m^2g^2k \sin(\omega t + \alpha) - \omega \cos(\omega t + \alpha)}{m^4g^4k^2 + \omega^2} \cos mg\xi, \quad (54e)$$

which is identical with the stationary term of (43)

(*b*). *The Evanescent Term, V.*

Let[1] $V = (Ae^{\beta x} + Be^{-\beta x})e^{\beta^2 t}$. (55)

As in the case of the stationary term, condition (*vii*) requires that

$$B = -A.$$

Condition (*viii*) requires that

$$A\beta(e^{\beta l} + e^{-\beta l})e^{\beta^2 kt} = 0 \text{ for all values of } t$$

which may be satisfied by setting

$$e^{\beta l} + e^{-\beta l} = 0, \text{ i. e. } e^{2\beta l} = -1, \text{ or } \beta l = \log \text{nat } i,$$

whence

$$\beta = \frac{(-1)^{n+1}(2n-1)i\pi}{2l}$$

where n is any positive integer. On substituting these values

[1] This use of the letter β is restricted to (55).

of B and β, (writing one term for each value of β) and converting into the trigonometrical form, (55) becomes

$$V = \sum 2A_n i(-1)^{n+1} e^{-\frac{(2n-1)^2\pi^2 kt}{4l^2}} \sin \frac{(2n-1)\pi x}{2l}, \quad (56a)$$

$$= \sum 2i(-1)^{\frac{m-1}{2}} A_n e^{-m^2g^2kt} \sin mgx, \quad (56b)$$

$$= \sum 2iA_n e^{-m^2g^2kt} \cos mg\xi, \quad (56c)$$

m being written for $2n - 1$, g for $\pi/2l$, and ξ for $l - x$.

But, by (ix)

$$\sum 2iA_n \cos mg\xi = \frac{-2Mk}{l} \sum \frac{m^2g^2k \sin \alpha - \omega \cos \alpha}{m^4g^4k^2 + \omega^2} \cos mg\xi. \quad (57)$$

Therefore,

$$V = \frac{-2Mk}{l} \sum \frac{m^2g^2k \sin \alpha - \omega \cos \alpha}{m^4g^4k^2 + \omega^2} e^{-m^2g^2kt} \cos mg\xi, \quad (58)$$

which is identical with the evanescent term of (43d) since $g^2k = a$.

(c) *The Complete Expression*, $S + V$

Thus from (54) and (58)

$$[\textit{For sinusoidal current}] \quad z - z_0 = S + V$$

$$= \frac{M}{\mu\sqrt{2}} \sqrt{(F^2 + G^2)(H^2 + J^2)} \,.\, \sin(\omega t + \alpha + \gamma - \tfrac{1}{4}\pi)$$

$$- \frac{2Mk}{l} \sum \frac{m^2a \sin\alpha - \omega \cos\alpha}{m^4a^2 + \omega^2} e^{-m^2at} \cos mg\xi. \quad (59)$$

Equation (59) is the "hyperbolic form" of (43).

Values of $z - z_0$ at the electrode may be obtained by replacing x by l (and consequently cos mgξ by unity). Thus, when the *stationary state* is reached

$$[\textit{Stat. at elec.}] \quad z - z_0 =$$

$$\frac{M}{2}\sqrt{\frac{k}{\omega}} \frac{\sqrt{\sinh^2 2\mu l + \sin^2 2\mu l}}{\sinh^2 \mu l + \cos^2 \mu l} \sin(\omega t + \alpha + \gamma - \tfrac{1}{4}\pi), \quad (60)$$

where

$$\mu = \sqrt{\frac{\omega}{2k}}$$

and

$$[at\ electrode]\ \gamma = \overline{tan}^{-1}\frac{sin\,2\mu l}{sinh\,2\mu l}. \qquad (61)$$

With increasing values of $l\mu$, cos $l\mu$ and sin $l\mu$ vanish in comparison with sinh $l\mu$, while sinh $2l\mu$ approaches equality with 2 sinh^2 $l\mu$. The value of the fraction $\frac{\sqrt{sinh^2 2l\mu + sin^2 2l\mu}}{sinh^2 l\mu + cos^2 l\mu}$ thus approaches 2, and the value of "γ at the electrode" (61) approaches zero. Thus from (60)

$$[For\ t = \infty,\ at\ electrode]\ z - z_0 = M\sqrt{\frac{k}{\omega}}\,sin\,(\omega t + \alpha - \tfrac{1}{4}\pi). \qquad (62)$$

The same results may be obtained by setting $\xi = 0$ in (46*c*); by means of (60), however, the limits within which the convenient equation (62) may be used can be ascertained. By looking up tables[1] of the hyperbolic functions it will be found that the substitution of (62) for (60) cannot introduce an error of more than one-half percent if $l\mu = l\sqrt{\frac{\omega}{2k}} \geqq 3$. Assuming $\omega = 377$ (*i. e.*, 60 cycles per second), and $k = 4 \times 10^{-6}$ (an average value) it follows that l is practically "infinite" for the purposes of this equation when it reaches 5×10^{-4} centimeters.

Amplitude

When the stationary state is reached, the values of z swing equally above and below z_0; the maximum values of $z - z_0$ being reached when $sin\ (\omega t + \alpha + \gamma - \frac{1}{4}\pi) = 1$. An expression for the "amplitude" may accordingly be found by substituting this value in the stationary term of (59), or in (60) if the amplitude at the electrode be sought. From (46*c*) it follows that when $l = \infty$ the amplitude at any point in the diffusion layer is $\frac{M}{2}\sqrt{\frac{k}{\omega}}\,e^{-\mu\xi}$.

Lag

The electric current is at its maximum when $\omega t + \alpha = \frac{1}{2}\pi$;

[1] Smithsonian Mathematical Tables; Hyperbolic Functions, Washington, published by the Smithsonian Institution 1909.

when the stationary state is reached, the concentration reaches its maximum whenever $\omega t + \alpha + \gamma - \frac{1}{4}\pi = \frac{1}{2}\pi$ (see Eq. 59). The difference, $\frac{1}{4}\pi - \gamma$, gives the phase difference or "lag" of the concentration wave behind the wave of current at the stationary state. The lag at the electrode may be found by computing γ from (61) and subtracting from $\pi/4$.

The angle γ is a function of $l\mu$ whose value rapidly falls off with increase in $l\mu$, while alternating in sign.

Illustration

As an illustration, a number of values of $(z - z_0)/M$ at the electrode have been computed for the case that $k = 4 \times 10^{-6}$, $l = 3.14 \times 10^{-4}$, $\omega = 377$ (60 cycles per second), and $\alpha = \frac{1}{2}\pi$ (*i. e.*, at the moment of throwing on the current, the latter is at its maximum). Fig. 9 gives a graph of the

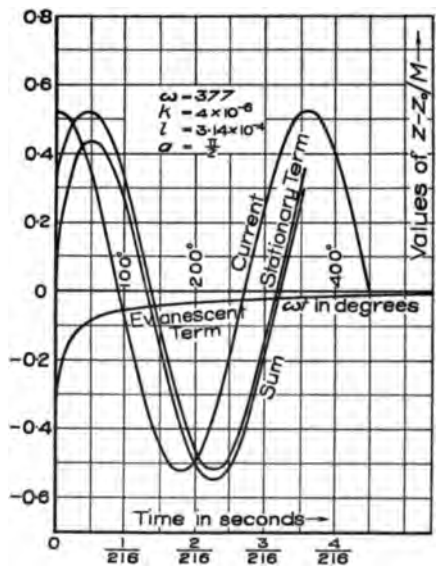
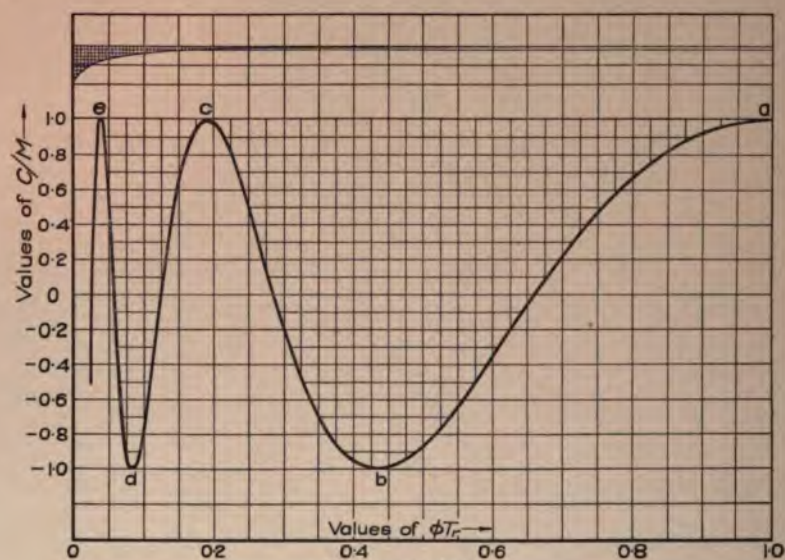


Fig. 9

evanescent term, of the stationary term, and of their sum, *i. e.*, the values of $(z - z_0)/M$ at the electrode. The "current" wave is drawn on an arbitrary scale to illustrate the

difference in phase, (lag). Figs. 10 and 11 apply to the same case; the areas *abc*, *cde*, etc., above the curve correspond to the expression within the { } brackets of (29*d*).



Figs. 10 and 11

Sec. 7.—Superposed Currents

Since all the equations of this Part satisfy the same "initial" condition and the same "solution" condition, and since the sum of a number of solutions of the linear differential equation (*iii*) is likewise a solution, the concentration changes produced by any number of currents acting simultaneously may be obtained by adding together the right hand members of the equations which give the concentration changes that would be produced by each current taken separately. Thus the effects produced by approximately sinusoidal currents could be computed if the current were analyzed in the ordinary way, and expressed as the sum of a pure sinusoidal current and its higher harmonics.

Other problems may be handled in the same way. Suppose, for instance, that the sinusoidal current for which $C = M \sin(\omega t + \alpha)$, and the direct current for which $C = C^1$

both enter the solution by the same electrode; when the stationary state is reached, the amplitude of the concentration variation at the electrode caused by the sinusoidal current alone would be

$$\frac{M}{2}\sqrt{\frac{k}{\omega}}\,\frac{\sqrt{sinh^2 2\mu l + sin^2 2\mu l}}{sinh^2 \mu l + cos^2 \mu l} \tag{63}$$

while that caused by the direct current alone would be zero; (63) thus gives the maximum deviation of z above and below the centre of swing. If the sinusoidal current acted alone, the centre of swing would be at $z = z_0$; if the direct current acted alone, the centre would be at $z = z_0 + C_1 l$; thus

$$C_1 l - \frac{M}{2}\sqrt{\frac{k}{\omega}}\,\frac{\sqrt{sinh^2 2\mu l + sin^2 2\mu l}}{sinh^2 \mu l + cos^2 \mu l} \tag{64}$$

gives the lowest value of $z - z_0$ reached at the electrode during electrolysis.

If the electrode were of silver, for instance, in a solution of copper sulphate practically free from silver (*i. e.*, $z_0 = 0$), the ratio between the two currents that would just prevent the concentration of the silver salt at the electrode from falling to zero during the cycle might be found by setting the expression (64) equal to zero and solving for $\sqrt{2}\, C_1/M$ (since the reading[1] on the alternating current ammeter is proportional to $M/\sqrt{2}$, and that on the direct current ammeter to C_1). This ratio is a function of $l^2\omega/k$, *i. e.*, of the time constant and of the duration of the cycle. If $k = 4 \times 10^{-6}$, $l = 3.14 \times 10^{-4}$ cm., and $\omega = 377$, the reading on the direct current ammeter would be 0.469 times that on the alternating.

If $\mu l \geqq = 3$, the *sinh* fraction in (64) is very closely equal to 2.00, and $C_1/M = \sqrt{k}/l\sqrt{\omega}$.

Measurements of this nature might prove an easy means

[1] In order that this may be true exactly as stated in the case under consideration it is necessary that the composite current be obtained synthetically from two separate circuits having the cell in their only common part. The alternating current ammeter must then be in the alternating current circuit and not in series with the cell.

of finding the ratio k/l^2; if a "limiting current" were likewise determined (see pg. 830) the two measurements would give both k and l.

PART II

THE REACTION AT THE ELECTRODE CHANGES WHEN z AT THE ELECTRODE ATTAINS THE VALUE ζ

At the cathode in an acid solution of copper sulphate, the concentration of the copper, z, decreases when the current is thrown on; all values of $z - z_0$ will therefore be negative, they may be computed by (15*c*) remembering that G as defined in the Introduction, and therefore C as defined by (8), are negative. The curves *oad* for $at = 0.25$, *obe* for $at = 0.35$, *ofg* for $at = 0.50$, and *oh* for $t = \infty$, in Fig. 12 were so obtained; they differ from the corresponding

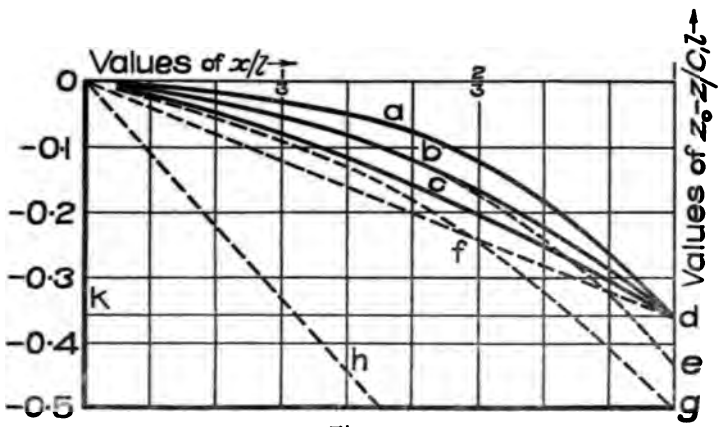


Fig. 12

curves in Fig. 1 only in scale, and in that $z - z_0$ is measured downward to indicate decrease in z as the electrode is approached.

As noted on pg. 832, (15*c*) merely fixes a relation between $(z - z_0)/Cl$, x/l, and at. irrespective of the absolute values of z, x, and t; the values of $(z - z_0)/Cl$ correspond to $z = 0$, and therefore the height in the figure of the horizontal line corresponding to $z = 0$, will vary from case to case. Assuming it to have the position given by *kd* in Fig.

12, z at the electrode will reach zero at $at = 0.25$; from that moment on, Eq. (15) which predicts still further fall in z (as indicated by the dotted lines *obe*, *ofg*, *oh*) ceases to be applicable, and must be replaced by another.

Sec. 8.—Constant Current

This new equation must be a solution of the differential equation (*iii*, Fick's law, pg. 820), it must also fulfil the "solution condition" (*i*, pg. 818), but the "electrode condition (*iv*, pg. 821) must be replaced by

$$[\textit{Electrode condition}]\ At\ x = l,\ and\ t > \vartheta,\ \partial z/\partial t = 0 \qquad (xi)$$

which says that from a certain value of t (*viz:* ϑ) onwards, the concentration at the electrode remains unaltered at the value ζ; at the cathode in the copper solution $\zeta = 0$.

The "initial condition" (*ii*, pg. 819) also must be replaced, by

$$[\textit{Condition at } t = \vartheta]\ z - z_0 = C_1 x - \frac{8C_1 l}{\pi^2} \sum \frac{1}{m^2} \cdot e^{-\frac{m^2\pi^2 k\vartheta}{4l^2}} \cdot \cos \frac{m\pi(l-x)}{2l} \qquad (xii)$$

signifying that at $t = \vartheta$, the values of z are those caused by the operation of the constant current C_1 for ϑ seconds.

From (1), introducing the special values of B_n and D from (3) and (4), and writing c instead of C_1, q instead of n and ρ instead of E_n to avoid confusion with the formulas of Part I, the equation

$$z - z_0 = cx + \sum_{q=1}^{\infty} A_q e^{-\rho^2 kt} \sin \rho x \qquad (65)$$

may be obtained, which satisfies (*iii*) and (*i*). To satisfy (*xi*) it is necessary that

$$\rho = \frac{q\pi}{l} \qquad (66)$$

as may be found by differentiating, etc., in the manner illustrated on pg. 823.

At the electrode, $z = \zeta$, and $x = l$, (hence $\sin \rho x = 0$) so that

$$c = \frac{\zeta - z_0}{l}. \qquad (67)$$

Introducing these values of ρ and c, (65) becomes

$$z - z_0 = \frac{\zeta - z_0}{l} x + \sum_{q=1}^{\infty} A_q e^{-\frac{q^2\pi^2 kt}{l^2}} \sin\frac{q\pi x}{l}. \tag{68}$$

and satisfies *i*, *iii*, and *xi*.

To introduce (*xii*), the two expressions for $z - z_0$ at the moment $t = \vartheta$ obtainable from (*xii*) and (68) may be equated; replacing $(\zeta - z_0)/l$ by its value from (*xii*), *viz.:*

$$\frac{\zeta - z_0}{l} = C_1 - \frac{8C_1}{\pi^2}\sum\frac{1}{(2n-1)^2}\cdot e^{-\frac{(2n-1)^2\pi^2 k\vartheta}{4l^2}}\cdot \cos\frac{(2n-1)\pi(l-x)}{2l} \tag{69}$$

and rearranging

$$\sum_{q=1}^{\infty} A_q e^{-\frac{q^2\pi^2 kt}{l^2}} \sin\frac{q\pi x}{l} =$$

$$-\frac{8lC_1}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{(2n-1)^2}\cdot e^{-\frac{(2n-1)^2\pi^2 k\vartheta}{4l^2}}\left(\cos\frac{(2n-1)\pi(l-x)}{2l} - \frac{x}{l}\right) \tag{70a}$$

$$= \frac{-8lC_1}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{(2n-1)^2}\cdot e^{-\frac{(2n-1)^2\pi^2 k\vartheta}{4l^2}}\sum_{q=1}^{\infty}\frac{2(2n-1)^2(-1)^q}{q\pi(\overline{2n-1}^2 - 4q^2)}\sin\frac{q\pi x}{l} \tag{70b}$$

(70*b*) being obtained by substituting an equivalent Fourier's series for the expression in brackets at the right of (70*a*) (see Appendix).

The value of A_q may now be found, for any fixed value of q, by removing the $\sum_{q=1}^{\infty}$ sign from both sides of (70*b*) and simplifying. Inserting the value so found in (68), there results:

$$z - z_0 = \frac{\zeta - z_0}{l} x +$$

$$\frac{16lC_1(-1)^{q+1}}{\pi^3}\sum_{n=1}^{\infty}\sum_{q=1}^{\infty}\frac{e^{-\frac{\pi^2 k}{4l^2}(4q^2 t - \vartheta + \overline{2n-1}^2\vartheta)}}{q(\overline{2n-1}^2 - 4q^2)}\cdot \sin\frac{q\pi x}{l} \tag{71}$$

which satisfies all four relations *i*, *iii*, *xi* and *xii*.

The symbol $\sum_{n=1}^{\infty}\sum_{q=1}^{\infty}$ signifies that the value of the expression on the right of (71) is to be computed for each value of q (for instance $q = 1$) combined with every value of n ($n = 1, 2, 3, \ldots$) in turn; then for the next value of q, ($q = 2$) combined with every value of n, and so on; the sum of all these results is to be used in finding $z - z_0$.

Equation (71) is applicable whenever, for any reason, the concentration z at the electrode remains constant after reaching a certain value ζ. The case $\zeta = 0$ is no doubt the commonest, but cases where $\zeta - z_0 > 0$ may perhaps be met with where the product of electrolysis crystallizes at the electrode thus forming a saturated solution there; other cases where ζ differs from zero may be sought in the electrolysis of solutions containing excess of a second salt whose decomposition voltage is only slightly greater than that of the salt to whose concentration z refers.

Illustration

In the case taken as illustration, ($\zeta = 0$, $a\vartheta = 0.25$) the constant current C_1 brings the concentration at the electrode from z_0 to zero in $0.25/a$ seconds; therefore, from (22*a*),

$$C_1 l = -2.784\, z_0.$$

Hence

[*for* $0 \leqq t \leqq 0.25$] $(z_0 - z)/z_0 =$

$$2.784\frac{x}{l} - 2.257\sum\frac{1}{m^2}e^{-m^2at}\cos mg\xi, \quad \text{(from 15c)}$$

and

[*for* $t \geqq 0.25$] $(z_0 - z)/z_0 =$

$$x/l - 1.436\,(-1)^q\sum_{n=1}^{\infty}\sum_{q=1}^{\infty}\frac{e^{-4q^2(at-0.25)-0.25\,m^2}}{q(m^2-4q^2)}\cdot\sin\frac{q\pi x}{l}, \quad \text{(from 71)}$$

whence,

At the points $x/l =$	0	0.25	0.50	0.75	1.00
[1] when $at = 0.35$, $(z - z_0)/C_1 l =$	0	0.039	0.097	0.208	0.359
[1] when $at = 0.50$, $(z - z_0)/C_1 l =$	0	0.058	0.138	0.237	0.359

[1] Corresponding values of $(z_0 - z)/z_0$ may be obtained by multiplying by 2.784.

These points determine the curves *obd* and *ocd* in Fig. 12; *ofd*, the straight line joining o and *d*, gives the concentrations at $t = \infty$.

Sec. 9.—Successive Currents

At some moment t ($t > \vartheta$), suppose that the current corresponding to C_1 is changed to a current corresponding to C_2. In the case chosen for illustration ($\zeta = 0$), if C_2 be numerically greater (algebraically less) than C_1, z at the electrode will remain equal to ζ; if C_2 lie between C_1 and the limiting current corresponding to ζ (*viz.*: $C' = (\zeta - z_0)/l$, Eq. 24) the concentration at the electrode will ultimately remain at ζ, although if $t - \vartheta$ be not too great it may momentarily rise above ζ and then fall again.

If, however, C_2 be (numerically) less than C', the concentration at the electrode will rise permanently above ζ. From the moment t_1 at which this change of current occurs, the following conditions will hold, *viz.*:

[*Fick's law*] $\partial z/\partial t = k\,\partial^2 z/\partial x^2$. (*iii*)
[*Solution condition*] For $x = 0$, $\partial z/\partial t = 0$. (*i*)
[*Electrode condition*] For $x = l$, $\partial z/\partial x = C_2$. (*iv*)
["*Initial*" *condition*] For $t = t_1$, $z - z_0$ = an expression obtainable by writing t_1 for t in (71). (*xiii*)

The first three may be complied with by setting $t = t_1$ in (1), and substituting the values of B_n, D and E_n given by (3), (4), and (7) respectively; v is written instead of n to avoid confusion with the first summation. To introduce the "condition at $t = t_1$" the expression on the right of (*xiii*) must be converted into a series proceeding by sines of odd multiples of $\pi x/2l$ (see Appendix); the A_v's may then be found in the usual way. On carrying out these operations there results:

$$[For\ t \gtrless t_1]\ z - z_0 = C_2 x + \frac{8l}{\pi^2}\left(\frac{\zeta - z_0}{l} - C_2\right)\sum_{n=1}^{\infty} e^{\frac{-m^2 a(t-t_1)}{m^2}} \cos mg\xi$$

$$- \frac{128\,C_1 l}{\pi^4}\sum_{n=1}^{\infty}\sum_{q=1}^{\infty}\sum_{v=1}^{\infty}\frac{e^{exp.}\cos(2v-1)\pi\xi}{(2n-1^2-4q^2)(2v-1^2-4q^2)}, \qquad (72)$$

where, as usual, $m = 2n - 1$, $g = \pi/2l$, $a = \pi^2k/4l^2$, $\xi = l - x$ and the exponent of e (indicated by "exp" in (72)) is

$$\frac{-\pi^2 k}{4l^2}[(2n-1)^2\vartheta + 4q^2(t_1 - \vartheta) + (2v-1)^2(t - t_1)]. \quad (73)$$

If $t_1 - \vartheta$ be very large, the exponential factor of the triple sum becomes zero, and only the first two terms of (72) remain. Large values of $t_1 - \vartheta$, however, correspond to a linear fall of concentration throughout the diffusion layer at the moment $t = t_1$; the single sum term of (72) can accordingly be deduced from (1), (3), (4), and (7) by introducing the condition.

$$[For\ t = t_1]\ z_0 - z = (z_0 - \zeta)x/l. \qquad (xiv)$$

in place of (*xiii*), or it may be derived from (31), the general equation for a cycle of two beats, by making $\theta_1 = \infty$ see; (32).

Illustration

If for instance the constant current corresponding to C_1 which brings the concentration at the electrode to zero at $at = 0.25$ (see preceding section) persist till $at = 0.50$, the values of $(z - z_0)/C_1l$ at the electrode from $at = 0$ to $at = 0.25$ will be given by points on the curve oa of Fig. 13, which except in scale and the direction in which $(z - z_0)/C_1l$ is measured, is identical with the first part of the curve of Fig. 3. From $at = 0.25$ to $at = 0.5$ the concentration will remain stationary at $z = 0$ (Fig. 13, line *ad*).

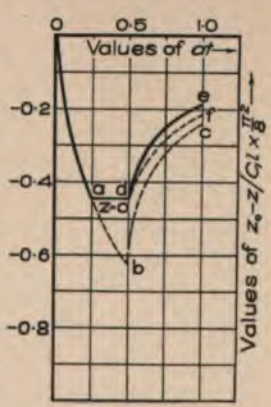


Fig. 13

Now let the current be shut off and be succeeded by a pause ($C_2 = 0$) lasting from $at = 0.50$ till $at = 1.0$, as in the "special case of interrupted currents" illustrated in Sec. 3. The concentrations at the electrode will rise, following the curve *de* of Fig. 13, points for which have been calculated by means of (72).

To show the effect of the new electrode condition (*xi*), the curve for $at = 0$ to $at = 1.0$ of Fig. 8 has been drawn again in Fig. 13; it is represented by the broken line *oabc*. The curve *df* (points for which were computed from the first two terms only of Eq. 72) gives the concentrations that would be found during the second beat, if the first current had persisted long enough to bring about a linear concentration gradient throughout the diffusion layer. The difference between *de* and *df* in Fig. 13 corresponds to that between *ocd* and *ofd* in Fig. 12.

An equation involving triple summation would suffice to trace the concentrations during the first part of the third beat, *i. e.*, until the concentration at the electrode again became zero; but each time the "electrode condition" changes from (*iv*) to (*xi*) or back again the order of the summation is increased by unity. Simplifications are introduced if one of the beats is of long duration; but in general it would probably be easier to plan experiments in which the conditions discussed in this Part are avoided, than to carry out the computations that would otherwise be necessary. Illustrations of how this may be accomplished are given in Part III.

PART III

SECONDARY REACTIONS

In Parts I and II of this paper all changes of concentration occurring in the solution during electrolysis have been ascribed to electrolytic migration and to the diffusion of the products of electrolysis from the electrode, or, as the case may be, to the diffusion toward the electrode of such of the constituents of the solution as were consumed at that point. It will now be assumed that, apart from the effect of diffusion, the concentrations of the products of electrolysis may be lowered by the occurence of "secondary" reactions, *i. e.*, reactions between the products of electrolysis and the other constituents of the solution; and the special assumption will be made that the rate at which such reac-

tions proceed is proportional to the concentration of the substance whose concentration is represented by z.

The rate of change of concentration of such a constituent at any point in the diffusion layer will therefore be represented by

$$[\textit{Differential equation}]\ \partial z/\partial t = k\,\partial^2 z/\partial x^2 - Kz, \qquad (xiv)$$

where K is the "velocity constant" of the secondary reaction. As is well known, K in general depends on the temperature, and on the concentrations of the other constituents of the solution, and even if these factors be kept constant many reactions have been discovered for which the rate is not proportional to the concentration of the disappearing substance; there are enough cases in which the rule holds, however, to make it worth discussion, while to assume that the rate might be proportional to any other than the first power of z would wholly change the nature of the differential equation.

The suggestion that the rates of such almost "instantaneous" reactions as that between copper salts and cyanides might be determined by electrolytic experiments is due to LeBlanc, who has already carried out a number of experiments from which the order of magnitude of such rates may be inferred. The following paragraphs suggest methods for determining K directly; if carried out at different temperatures and with different concentrations of the other reagents, the effect of these factors on the rate of the reaction might also be determined.

To simplify the discussion, it will further be assumed that the secondary reaction is practically "complete," *i. e.*, leads in time to the total destruction of the primary product of the electrolysis; thus the z_0 of Parts I and II becomes zero, and conditions (*i*) and (*ii*) are replaced by

$$[\textit{Solution condition}]\ \textit{At } x = 0,\ z = 0 \textit{ for all values of } t \qquad (xv)$$

$$[\textit{Initial condition}]\ \textit{At } t = 0,\ z = 0 \textit{ for all values of } x \qquad (xvi)$$

while the electrode condition remains the same as before

$$[\textit{Electrode condition}]\ \textit{At } x = l,\ \partial z/\partial x = G/k = C. \qquad (iv)$$

Sec. 10.—Constant Current

The "stationary term" of the new equation may be found by setting $\partial z/\partial t = 0$ in (*xiv*), whence

$$[At\ t = \infty] \quad 0 = k.d^2z/dx^2 - Kz \tag{74}$$

the solution of which is

$$z = A_1 cosh\, bx + A_2 sinh\, bx,\ where\ b = \sqrt{K/k}. \tag{75}$$

Condition (*xv*) leads to $A_1 = 0$, and (*iv*) to

$$A_2 = C/(b cosh\ bl),$$

so that the stationary term becomes

$$[For\ t = \infty \quad z = C\ sinh\, bx/(b\ cosh\ bl.) \tag{76}$$

The evanescent term, which must satisfy (*xiv*) and (*xv*), and for which at the electrode $\partial z/\partial x$ must equal zero (so as not to interfere with *iv*), may be derived from the form

$$\sum_{n=1}^{\infty} A_n\, e^{-(K+m^2a)t} \cos \frac{(2n-1)\pi(l-x)}{2l} \tag{77}$$

by determining the coefficients A_n so that at $t = 0$ the sum of stationary and evanescent terms will vanish, *i. e.*, so that

$$\sum_{n=1}^{\infty} A_n \cos \frac{(2n-1)\pi(l-x)}{2l} = -\frac{C\,.\,sinh\, bx}{b\,.\,cosh\, bl}. \tag{78}$$

This is accomplished (as illustrated in Secs. 1 and 8) by expanding the hyperbolic expression as a series of sines of $m\pi x/2l$, and introducing in (78).

Combining stationary and evanescent terms, the solution of (*xiv*) which satisfies (*xv*), (*xvi*), and (*iv*) is found to be

$$z = \frac{C\ sinh\, bx}{b\ cosh\, bl} - \frac{2kC}{l} \sum \frac{e^{-\psi t}}{\psi} \cos mg\xi \tag{79}$$

where C, k, l, t, x, have the meanings implied in (*xiv*), (*xv*) (*xvi*) and (*iv*) and explained at length in the Introduction and Part I; $m = (2n-1)$, $g = \pi/2l$, $\xi = l - x$, $b = \sqrt{K/k}$, and ψ is written for $K + m^2a = K + (2n-1)^2\pi^2k/4l^2$.

$\sum$ is used for $\sum_{n=1}^{\infty}$. An expression for the concentrations at the electrode may be obtained by setting $x = l$ in (79).

$$[For\ x = l] \quad z = \frac{C}{b} \tanh bl - \frac{2kC}{l} \sum \frac{e^{-\psi t}}{\psi}. \qquad (80)$$

On consulting tables of the hyperbolic functions, it will be found that when $bl \leq 0.15$, *tanh bl* may be replaced by bl with an error not exceeding eight-tenths of one percent; the stationary term then becomes Cl as in (15). Assuming $k = 4 \times 10^{-6}$ as in the former illustrations, $bl = l\sqrt{K/k} \leq 0.15$ implies $K \leq 0.09$ when $l = 10^{-3}$ cm, and $K \leq 9.0$ when $l = 10^{-4}$ cm. Perhaps the highest values of K that can be measured satisfactorily by the direct methods of chemical kinetics[1] do not exceed $K = 0.09$, corresponding to a fall of the concentration to one half its original value every eight seconds, thus if the secondary reaction takes place at any ordinarily measurable rate, the stationary term of (80) becomes Cl.

On the other hand, when $bl \geq 3.0$, *tanh bl* may be replaced by unity with an error not exceeding one-half percent; and the stationary term of (80) becomes $C\sqrt{k/K}$, $= G/\sqrt{Kk}$. Assuming $k = 4 \times 10^{-6}$ as before, this gives $K \geq 36$ if $l = 10^{-3}$ cm, and $K \geq 3600$ if $l = 10^{-4}$ cm as the values that must be reached by K if this approximation is to be employed.

Erf approximation. Evaluation of the evanescent part of (80) by simple addition of the terms is quite impossible when K is large, on account of the slow convergence; if at be small, however, an approximately equivalent expression, based on the equation of Thomson and Cayley (Eq. 18) may be employed.

Writing

$$\frac{2kC}{l} \sum_{n=1}^{\infty} \left(\frac{e^{-(K+m^2a)t}}{K+m^2a} - \frac{1}{K+m^2a} \right) =$$

$$-\frac{2kC}{l} \sum_{n=1}^{\infty} \int_0^t e^{-(K+m^2a)t}\, dt = -\frac{2kC}{l} \int_0^t \left(e^{-Kt} \sum_{n=1}^{\infty} e^{-m^2at}\right) dt \quad (81)$$

[1] Such a case was studied by Miss Benson, Jour. Phys. Chem., **7**, 356 (1903).

the summation in the last expression may be replaced by its approximate value (*viz.:* $\frac{1}{4}\sqrt{\frac{\pi}{at}}$) from (20), and the term $\frac{2kC}{l}\sum\frac{1}{K+m^2a}$ by its equivalent *viz.:* $\frac{C}{b}$ *tanh bl*, so that

$$\frac{C}{b}\tanh bl - \frac{2kC}{l}\sum\frac{e^{-\psi t}}{\psi} = \textit{(approximately)}$$

$$\frac{kC}{2l}\sqrt{\frac{\pi}{a}}\int_0^t e^{-Kt}t^{-\frac{1}{2}}\,dt = \frac{2C}{b\sqrt{\pi}}\int_0^{\sqrt{Kt}} e^{-y^2}\,dy, \quad (82)$$

and equation (80) reduces to

$$[\textit{For at small}] \quad z = \frac{2C}{b\sqrt{\pi}}\int_0^{\sqrt{Kt}} e^{-y^2}\,dy = \frac{G}{\sqrt{kK}}\frac{2}{\sqrt{\pi}}\,Erf\sqrt{kt}. \quad \textit{approx.} \quad (83)$$

Values of the "probability integral," $\frac{2}{\sqrt{\pi}}\,Erf\,y = \frac{2}{\sqrt{\pi}}\int_0^y e^{-y^2}\,dy$ are tabulated in most books on Least Squares;[1] when the argument is zero, the probability integral is likewise zero, and the integral reaches 0.99 when the argument reaches 1.8; the maximum value of the integral is unity.

Sec. 11.—Successive Currents in General

To obtain an expression for the concentrations when a current corresponding to C_1, after passing for the interval $t = 0$ to $t = t_1$, is succeeded by a current corresponding to C_2 which persists from $t = t_1$ to $t = t_2$, and so on, as described in Sec. 2, (79) may be written

$$[\textit{For } t = t_1] \quad z = \frac{C_2 \sinh bx}{b\cosh bl} - (C_2 - C_1)\frac{\sinh bx}{b\cosh bl} - \frac{2k}{l}\sum\frac{C_1}{\psi}\cdot e^{-\psi t_1}\cdot\cos mg\xi, \quad (84a)$$

$$= \frac{C_2\sinh bx}{b\cosh bl} - \frac{2k}{l}\sum\frac{1}{\psi}(C_1e^{-\psi t_1} + C_2 - C_1)\cos mg\xi. \quad (84b)$$

[1] For instance, Merriman and Johnson each give a four-place table, while Bertrand (*Calcul des Probabilités*) and De Morgan (*On Probabililies*) each give a seven-place table, the argument in each case advancing by 0.01. A far more elaborate table in which the argument advances generally by 0.001 is given by Burgess *Trans. Edin. Roy. Soc.*, 39, 257 (1899).

Proceeding as indicated in Sec. 2, the general expression for the concentrations during the pth beat may be obtained:

$$[For\ t_{p-1} \leqq t \leqq t_p] \quad z = C_p \frac{\sinh bx}{b \cosh bl} - \frac{2k}{l} \sum_{n=1}^{\infty} \frac{1}{\psi} \Big\{ C_1 e^{-\psi t} + \sum_{r=2}^{p} (C_r - C_{r-1}) e^{-\psi(t-t_{r-1})} \Big\} \cos mg\xi, \quad (85a)$$

$$= C_p \frac{\sinh bx}{b \cosh bl} - \frac{2k}{l} \sum_{n=1}^{\infty} \frac{1}{\psi} \Big\{ C_p \Phi T_{p-1} + \sum_{r=1}^{p-1} C_r (\Phi T_{r-1} - \Phi T_r) \Big\} \cos mg\xi, \quad (85b)$$

where

$$T_r = t - t_r, \text{ and } \Phi T_r = e^{-\psi(t-t_r)},$$

whence the expressions for the concentrations during the progress of odd and even beats in two-beat cycles:

$$[For\ p\ odd]\ z = \frac{C_1 \sinh bx}{b \cosh bl} + \frac{2k}{l}(C_2 - C_1) \sum \frac{e^{-\psi r}}{\psi} \cdot \frac{e^{\psi\theta} - e^{\psi\theta_1}}{e^{\psi\theta} - 1} \cos mg\xi - \frac{2k}{l} \sum \frac{e^{-\psi t}}{\psi} \Big\{ C_1 + (C_2 - C_1) \frac{e^{\psi\theta} - e^{\psi\theta_1}}{e^{\psi\theta} - 1} \Big\} \cos mg\xi. \quad (86)$$

$$[For\ p\ even]\ z = \frac{C_2 \sinh bx}{b \cosh bl} + \frac{2k}{l}(C_1 - C_2) \sum \frac{e^{-\psi r}}{\psi} \cdot \frac{e^{\psi\theta} - e^{\psi\theta_2}}{e^{\psi\theta} - 1} \cos mg\xi - \frac{2k}{l} \sum \frac{e^{-\psi t}}{\psi} \Big\{ C_1 + (C_2 - C_1) \frac{e^{\psi\theta} - e^{\psi\theta_1}}{e^{\psi\theta} - 1} \Big\} \cos mg\xi. \quad (87)$$

From (86) and (87) expressions for the amplitude and for the concentration at the centre of swing in the case of two-beat cycles may be obtained (see pg. 839); they are:

$$[Amplitude] \quad \tfrac{1}{2}(C_1 - C_2) \frac{\sinh bx}{b \cosh bl} + \frac{k}{l}(C_1 - C_2) \sum \frac{1}{\psi} \cdot \frac{e^{\psi\theta_1} + e^{\psi\theta_2} - 2e^{\psi\theta}}{e^{\psi\theta} - 1} \cos mg\xi. \quad (88)$$

$$[At\ centre] \quad z = \tfrac{1}{2}(C_1 + C_2) \frac{\sinh bx}{b \cosh bl} + \frac{k}{l}(C_1 - C_2) \sum \frac{1}{\psi} \cdot \frac{e^{\psi\theta_1} - e^{\psi\theta_2}}{e^{\psi\theta} - 1} \cos mg\xi. \quad (89)$$

When θ_1 and θ_2 are very large, the concentrations at any point in the diffusion layer oscillate between $(C_1 \sinh bx)/(b \cosh bl)$ and $(C_2 \sinh bx)/(b \cosh bl)$; when θ is very small, the amplitude is practically zero, and the concentration at the centre of swing is $\left(C_1 \frac{\theta_1}{\theta} + C_2 \frac{\theta_2}{\theta}\right) \sinh bx/(b \cosh bl.)$

Sec. 12.—Simple Alternating Current

If the current corresponding to C_1 pass for θ_1 seconds through a copper electrode into a solution of potassium cyanide, making the copper anode, and if then the current corresponding to C_2 make the copper cathode for the same interval θ_1 seconds, and be succeeded by C_1 for θ_1 seconds and so on; the ratio between the two currents that will just bring the concentration at the electrode to zero at the end of the cathode beats when the stationary state has been reached, may be found by setting $x = l$, $t = \infty$, $z = 0$, $\tau = 0$, and $\theta = 2\theta_1$ in (86).

Making these substitutions, and dividing the numerator of the θ fraction by its denominator, the result may be put in the form

$$\frac{C_1}{C_1 - C_2} = \frac{2kb}{l \tanh bl}\left\{\sum \frac{1}{\psi} - \sum \frac{e^{-\psi\theta_1}}{\psi} + \sum \frac{e^{-2\psi\theta_1}}{\psi} - \sum \frac{e^{-3\psi\theta_1}}{\psi} + etc.,\right\} \quad (90)$$

and if $a\theta_1$ be small enough to justify the use of the Erf approximation,

$$\frac{C_1}{C_1 - C_2} = 1 - [1 - (\coth bl) \frac{2}{\sqrt{\pi}} Erf \sqrt{K\theta_1}] + [1 - (\coth bl) \frac{2}{\sqrt{\pi}} Erf \sqrt{2K\theta_1}] - etc. \quad (91)$$

For high values of $l\sqrt{\frac{K}{k}}$, $\coth bl$ becomes unity, and the ratio between the two currents is independent of k and of l, becoming in fact a function of $K\theta_1$.

In making an actual computation, $\frac{2k}{l}\sum \frac{1}{\psi}$ would be re-

placed by its value $(\tanh bl)/b$ and the Erf approximation would be used for the first few summations of (90) where direct summation would be too laborious; for higher values of the negative exponent, however, where the Erf approximation becomes less reliable, direct summation is easy.[1]

As an example, if $k = 4 \times 10^{-6}$, $l = 3.1416 \times 10^{-4}$, $K = 400$, and the duration of each beat $\theta_1 = 0.0005$ seconds, the two currents would stand in the ratio of 68.97 to 31.03 or $G_2 = -0.4499\ G_1$.

If C_1/C_2 were determined in the laboratory, K could be found by (90) and (91); the easiest way, no doubt, would be to compute C_1/C_2 for a number of assumed values of K, plot the results, and find K from the observed C_1/C_2 by interpolation. If, however, in the experimental work, the currents in the two beats had been equal, and if it were attempted to calculate K from an experimental determination of the relative amounts of copper dissolved during the anode beat and redeposited during the cathode beat (*i. e.*, from the net loss of weight of the electrode)[2] or from an oscillographic determination of the moment during the cathode beat at which the concentration at the electrode fell to zero, the problem would become analogous to those of Part II; multiple summations would have to be employed, and the computations would become complicated and laborious.

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[1] When $\theta_1 = 0.0005$ and $a = 100$, the following are the true values and the Erf approximations respectively of the sums in (90), beginning with the first containing an exponential factor:

Number	1	2	3	4
True value	0.0020552	0.0014426	0.0010587	0.0007939
Erf approx.	0.0020552	0.0014426	0.0010587	0.0007939
Number	5	6	7	8
True value	0.0006031	0.0004619	0.0003557	0.0002749
Erf approx.	0.0006031	0.0004618	0.0003555	0.0002745

In the case of the last term mentioned in this table, which involves $e^{-8\psi\theta_1}$, the first two terms only of the summation suffice for the determination of five significant figures and the Erf approximation can thus in this case be dispensed with before it becomes inaccurate.

[2] As, for instance, in LeBlanc's experiments.

The quantity of cuprion[1] per square centimeter of electrode area left in the diffusion layer at the end of the cathode beat, *viz.:*

$$\int_0^l z dx = \frac{C_1 k(1 - sech\, bl)}{K} + \frac{4k}{\pi}(C_2 - C_1)\left[\sum \frac{(-1)^{n+1}}{m\psi} - \sum \frac{(-1)^{n+1} e^{-\psi\theta_1}}{m\psi} + \sum \frac{(-1)^{n+1} e^{-2\psi\theta_1}}{m\psi} \text{ etc.}\right] \quad (92)$$

is by no means negligible; in the case taken as illustration it amounts to $4.5099 \times 10^{-4}\ G_1$, as against $5.000 \times 10^{-4}\ G_1$ equivalents brought into the solution during an anode beat (the sum of the series in square brackets in (92) is 0.0009931, and $C_2 = -0.4499\ C_1$).

This is why an estimation of K from the experimentally determined ratio C_1/C_2, based on the rough and ready hypothesis that diffusion may be altogether neglected, and that at the end of the cathode beat (when $z = 0$ at both ends of the diffusion layer) the amount of cuprion in the diffusion layer may be neglected, leads to results very wide of the mark.[2]

The number of equivalents of cuprion that pass out from the diffusion layer into the body of the solution, per sq. cm of electrode surface, during an anode beat, may be found by multiplying the concentration gradient at the solution (at $x = 0$) by $k.d\tau$ and integrating:

$$k\int_0^{\theta_1}\left(\frac{\partial z}{\partial x}\right)_{x=0} d\tau = \frac{C_1\theta_1}{cosh\, bl} - \frac{k\pi}{l^2}(C_2 - C_1)\sum \frac{m}{\psi^2}\frac{(-1)^{n+1}}{1 + e^{-\psi\theta_1}}(e^{-\psi\theta_1} - 1). \quad (93)$$

A similar expression for the cathode beat may easily be obtained. In the case taken for illustration these quantities are not large. An approximate value for the loss during the cycle may be found, without summing the series of (93), by assuming that the loss would be the same as that caused by a constant current of average strength, $C = \frac{1}{2}(C_1 + C_2) = 0.275\ C_1$, acting throughout the cycle.

[1] Copper not combined with cyanide is meant.

[2] See under the next heading.

Using the formula for the stationary state (Eq. 76) this gives

$$k\int_0^{\theta_1}\left(\frac{\partial z}{\partial x}\right)_{x=0} d\tau = \frac{0.275 C_1 k\theta}{\cosh bl} \text{ approximately, } = 0.237 \times 10^{-4} G_1. \quad (94)$$

The loss from the diffusion layer during a complete cycle ($\theta = 2\theta_1 = 0.001$ seconds) is thus about five percent of that dissolved from the electrode during an anode beat.

Approximate Calculation of K from the Current Ratio

The quantity of cuprion in the diffusion layer opposite each sq. cm of electrode surface, (which in this paragraph only will be represented by y), is thus subject to change by the operation of three causes. It is being added to by electrolysis at the rate of G equivalents per second, it is being diminished by the chemical action of the cyanide at the rate of Ky equivalents per second, and there is a loss (which being small may be treated as constant throughout the cycle) of L equivalents per second into the main body of the solution.

Thus

$$[\text{Anode beat}]\frac{dy}{d\tau} = G_1 - Ky - L; \; [\text{Cathode beat}]\frac{dy}{d\tau} = G_2 - Ky - L. \quad (95)$$

Integrating between the limits 0 and θ_1, and θ_1 and $2\theta_1$, respectively, and writing w for the number of equivalents of cuprion remaining in the diffusion layer at the end of a cathode beat ($\tau = 0$, or $\tau = 2\theta_1$), there results

$$Kw = G_1 - L - (G_1 - G_2)\frac{e^{K\theta_1}}{e^{K\theta_1} + 1}. \quad (96)$$

Inserting the values found in the previous paragraph, *viz.:* $G_2 = -0.4499 G_1$, $w = 4.5099 \times 10^{-4} G_1$, and $L = 0.0237\, G_1$, Eq. (96) gives $K = 398$ in place of the true value $K = 400$.

Suppose, however, that the current ratio had been determined experimentally, and that it was proposed to calcu-

late K without taking account of diffusion at all, *i. e.*, from

$$-G_2/G_1 = e^{-K\theta_1} \qquad (97)$$

which may be obtained from (96) by setting $w = 0$ and $L = 0$, the wholly erroneous result K = 1597 would be obtained. The error is mainly due to neglecting w; if in (96) w be given its true value and L be set equal to zero, K comes out equal to 435.

Conditions Connoted by Large Values of $l\sqrt{\frac{K}{k}}$

During the discussion of (91) it was pointed out that when $l\sqrt{\frac{K}{k}}$ is large, C_1/C_2 is independent of k and l; according to (96), however, the current ratio can be independent of k and l only when the amount of cuprion left in the diffusion layer at the end of a cathode beat is likewise independent of the same two variables. The following considerations may help to make the reason for these relations clear.

If in any series of experiments z remains constantly zero at any fixed point in the solution, that point might be taken as $x = 0$, *i. e.*, its distance from the electrode might be taken as l; to keep $z = 0$ at any point *further* from the electrode could have no effect on the diffusion, and consequently to give l any *greater* value in any system of equations applicable to the case could have no effect on the results of the computations. By lessening k or increasing K the point at which z remains practically equal to zero is brought nearer to the electrode; and it follows from what has just been said, that when once it is nearer than the point selected as "$x = 0$" for the given system, the "solution condition" is without effect. Large values of t bring the evanescent terms to zero, and thus destroy the influence of the "initial condition;" if both circumstances occur together, the only equations influencing the result are the "differential equation" and the "electrode condition," which for any given value of k, *viz.*: k_1 may be written

$$\frac{\partial z}{\partial t} = k_1 \frac{\partial^2 z}{\partial \xi^2} - Kz \ (xiva); \qquad k_1 \frac{\partial z}{\partial \xi} = -G \qquad (iv\ a)$$

Suppose that in two cases the diffusion constants are k_1 and $k_2 = k_1/r^2$, respectively, where r is any constant multiplier. Replacing k_1 in (*xiv a*) and (*iv a*) by k_1/r^2 the equations for the second case will be

$$\frac{\partial z}{\partial t} = k_1 \frac{\partial^2 z}{\partial (r\xi)^2} - Kz; \quad k_1 \frac{\partial z}{\partial (r\xi)} = -rG \tag{98}$$

and it is obvious that (if conditions are such that the "initial" and "electrode" conditions may be neglected) the same values of z will be met with in both cases if $r\xi$ and rG in the second case have the same values as ξ and G in the first case, respectively; that is, when the current, and the distance from the electrode, of the points compared, are both r times less in the second case than in the first. Consequently (since, other things being equal, z is proportional to G) if the currents be *equal* in the two cases, the values of z at comparable points will be r *times greater* in the second case than in the first.

Hence, if the diffusion layer be imagined to be divided into corresponding laminae in the two cases, these being r times as thin in the second case as in the first and having concentrations r times greater, each will contain the same quantity of the component to which z refers. Further as explained above since the values of z in both cases fall to zero with increasing ξ and remain at zero, the impaired laminae having zero values of z will not affect the total, and therefore the total quantity of the component in the two cases being the sum of the same items must be the same. That is to say, the number of equivalents contained in the diffusion layer will be under these conditions independent of K.

Conditions that keep $z = 0$ at $\xi < l$ obviously prevent all loss from the diffusion layer into the main body of the solution, by destroying the concentration gradient at $\xi = l$; for large values of $l\sqrt{\frac{K}{k}}$ therefore, the integral expanded in (93) must reduce to zero.

Sec. 13.—[1]Sinusoidal Currents, Fourier Form

The general expression where $C = f(t)$, from which the expression for the sinusoidal current may be derived as a special case is:

$$z = \frac{\sinh bx}{b \cosh bl} f(t) - \frac{2k}{l} \sum_{n=1}^{\infty} \left\{ \frac{f(t)}{\psi} e^{-\psi t} \int_0^t e^{\psi u}.f(u).du \right\} \cos mg\xi. \quad (99a)$$

$$= \frac{2k}{l} \sum_{n=1}^{\infty} \left\{ e^{-\psi t} \int_0^t e^{\psi u}.f(u).du \right\} \cos mg\xi. \quad (99b)$$

Setting $f(t) = M \sin (\omega t + \alpha)$, this becomes

$$z = M \sin(\omega t + \alpha) \frac{\sinh bx}{b \cosh bl}$$

$$- \frac{2kM\omega}{l} \sum \frac{1}{\psi} \frac{\omega \sin(\omega t + \alpha) + \psi \cos (\omega t + \alpha)}{\psi^2 + \omega^2} \cos mg\xi$$

$$- \frac{2kM}{l} \sum e^{-\psi t} \frac{\psi \sin \alpha - \omega \cos \alpha}{\psi^2 + \omega^2} \cos mg\xi. \quad (100a)$$

$$= \frac{2kM}{l} \sum \frac{\psi \sin(\omega t + \alpha) - \omega \cos(\omega t + \alpha)}{\psi^2 + \omega^2} \cos mg\xi$$

$$- \frac{2kM}{l} \sum e^{-\psi t} \frac{\psi \sin \alpha - \omega \cos \alpha}{\psi^2 + \omega^2} \cos mg\xi. \quad (100b)$$

Where the harmonic analysis of a current is known it can be seen that for each component of the current there will be in the value of z a term expressible either in this form or in that of the next section.

Sec. 14.—Sinusoidal Currents, Hyperbolic Form

As in Part I, the stationary term may be expressed in a form more suitable for computation by the use of hyperbolic functions.

Starting out from (48), and introducing the new conditions, it will be found that the values obtained for A and B are those given by (49), but that the exponents γ and λ must be defined as follows:

[1] With regard to the applicability of these results see under Sec. 15.

$$\gamma^2 k = K + i\omega \text{ and } \lambda^2 k = K - i\omega, \tag{101a}$$

whence

$$\gamma = \beta + \delta i \text{ and } \lambda = \beta - \delta i, \tag{101b}$$

where

$$\beta^2 + \delta^2 = \frac{\sqrt{K^2 + \omega^2}}{k}, \beta^2 - \delta^2 = K/k, \text{ and } 2\beta\delta = \omega/k. \tag{101c}$$

Introducing these values in (48), the following expression for the stationary term is obtained

$$z = \frac{Mk^{\frac{1}{2}}}{(K^2 + \omega^2)^{\frac{1}{4}}} \cdot \frac{\sqrt{\cosh^2 x\beta - \cos^2 x\delta}}{\sqrt{\cosh^2 l\beta - \sin^2 l\delta}} \cdot \sin \chi \tag{102}$$

where

$$\chi = \omega t + \alpha + \tan^{-1}(\coth x\beta \,.\, \tan x\delta) - \tfrac{1}{2}\tan^{-1}(\omega/K), \\ - \tan^{-1}(\tanh l\beta \,.\, \tan l\delta). \tag{103}$$

On setting $K = 0$ in (102) it is reduced to (54); on setting $\omega = 0$ it is reduced to (76); and by means of suitable expansions of the hyperbolic functions it may be converted into the "Fourier" form, (stationary term of equation 100).

The evanescent term may be obtained from the general form

$$\sum_1^\infty A_n \frac{1}{\psi} e^{-\psi t} \cos mg\xi, \tag{104}$$

(which satisfies (*xiv*), (*xv*), and the condition that when $x = l$, $\partial z/\partial t = 0$), by expanding (102) in a series of sines of $mg\xi$ and determining the values of A_n as in sec. (6*b*). The resulting evanescent term is identical with that of (100).

Combining both terms, the "hyperbolic form" of the expression for sinusoidal currents becomes:

$$z = \frac{Mk^{\frac{1}{2}}}{(K^2 + \omega^2)^{\frac{1}{4}}} \cdot \frac{\sqrt{\cosh^2 x\beta - \cos^2 x\delta}}{\sqrt{\cosh^2 l\beta - \sin^2 l\delta}} \sin \chi \\ - \frac{2Mk}{l} \sum_{n=1}^\infty e^{-\psi t} \frac{\psi \sin \alpha - \omega \cos \alpha}{\psi^2 + \omega^2} \cos mg\xi \tag{105}$$

in which χ has the meaning given in (103), and β and δ those implied in (101*c*).

An expression for the *amplitude* at the stationary state may be found by setting $\sin \chi = 1$; the concentration at the centre of swing is zero. The "*lag*" is given by

$$[Lag] \tan^{-1}(\tanh l\beta . \tan l\delta) + \tan^{-1}(\omega/K) - \tan^{-1}(\coth x\beta . \tan x\delta). \quad (106)$$

Concentrations at the electrode may be found by substituting l for x in (105); in the evanescent term, this has the effect of making $\cos mg\xi$ unity, while the stationary term becomes

$$[For\ t = \infty,\ x = l]\quad z = \frac{Mk^{\frac{1}{2}}}{2(K^2 + \omega^2)^{\frac{1}{2}}} \frac{\sqrt{\sinh^2 2\beta l + \sin^2 2\delta l}}{\sinh^2 \beta l + \cos^2 \delta l} \sin \chi \quad (107)$$

where

$$\chi = \omega t + \alpha + \tan^{-1} \frac{\sin 2l\delta}{\sinh 2l\beta} - \tfrac{1}{2} \tan^{-1} \left(\frac{\omega}{K}\right). \quad (108)$$

If $\beta l \geqq 3$, $\sinh \beta l$ becomes $\geqq 10$, and the circular functions may be neglected in comparison with the hyperbolic. The fraction then becomes $\sinh 2\beta l / \sinh^2 \beta l$ which for values of $\beta l \geqq 3$ is very nearly equal to 2.00; thus (with a maximum possible error of one-half percent), when the stationary state is reached

$$[For\ x = l,\ \beta l \geqq 3]\quad z = \frac{Mk^{\frac{1}{2}}}{(K^2 + \omega^2)^{\frac{1}{2}}} \sin \chi . \quad (109)$$

Sec. 15.—Superposed Currents

As in Part I, the effect of a number of currents acting simultaneously may be found by adding the right hand members of the equations which express the effects of each of them alone. In fact, the assumption made throughout this Part, that $z_0 = 0$, deprives many of the equations of their validity unless when thought of as parts of such a sum; according to (107), for instance, the concentrations at the electrode would be *negative* during a large part of the cycle on electrolysis with a pure sinusoidal current.

When the stationary state has been reached during electrolysis with a sinusoidal current, the amplitude of the concentration variation at the electrode may be found by setting $\sin \chi_l = 1$ in (107). The centre of swing is zero with the sinusoidal current alone, but it may be raised to any desired

height, $C_1 \frac{\tanh bl}{b}$, by superposing the direct current corresponding to C_1. If $C_1 \frac{\tanh bl}{b}$ be greater than the amplitude, z at the electrode will never fall to zero; and the condition that z just touches zero once in the cycle is expressed by

$$0 = \frac{C_1}{b} \tanh bl - \frac{Mk^{\frac{1}{2}}}{2(K^2 + \omega^2)^{\frac{1}{4}}} \sqrt{\frac{\sinh^2 2\beta l + \sin^2 2\delta l}{\sinh^2 \beta l + \cos^2 \delta l}} \qquad (110)$$

whence the ratio of the two ammeter readings $\frac{C_1\sqrt{2}}{M}$ may be found:

$$\frac{C_1}{M} = \frac{1}{2} \frac{b}{\tanh bl} \frac{k^{\frac{1}{2}}}{(K^2 + \omega^2)^{\frac{1}{4}}} \sqrt{\frac{\sinh^2 2l\beta + \sin^2 2l\delta}{\sinh^2 l\beta + \cos^2 l\delta}}\,; \qquad (111)$$

the limit of (111) for $K = 0$ is the expression obtainable by equating (64) to zero.

With the ordinary alternating current of 60 cycles per second, $\omega = 377$; assuming $k = 4 \times 10^{-6}$, $l = 3.14 \times 10^{-4}$, and $K = 500$, the ratio C_1/M will be 0.912, and the ratio of the ammeter readings, 1.290 provided the arrangement is as described in the footnote to Sec. 7.

The ratio is a function of $l\sqrt{\frac{\omega}{k}}$ and $\frac{\omega}{K}$ so that if it be determined experimentally, and if in addition ω and a be known, K may be calculated. As the value of C_1 for which z at the electrode just touches zero should be recognizable by voltmeter or oscillograph or by weighing the electrode, (111) should lead to a convenient experimental method of determining the velocity constants of rapid "secondary" reactions. The ratio C_1/M will vary from the value discussed in Sec. 7 when K is zero, to 1 when K increases without limit (the value 1 would imply, in the case of a copper electrode in cyanide solution, that the copper never became cathode). Other things being equal, increasing ω brings the ratio nearer zero.

For large values of K, *tanh bl* becomes unity, and the *sinh* fraction of (111) reduces to 2.0; in this case the relation be-

tween the current ratio and the value of K takes the simple form

$$\left(\frac{C_1}{M}\right)^4 = \frac{K^2}{K^2 + \omega^2}, \tag{112}$$

and K may be determined without knowledge of k or l.

APPENDIX

Note on the Construction of Special Trigonometrical Series to Represent Arbitrary Functions

If it be required to express a given function of x, $f(x)$, between given values of x as the sum of a series of sines and cosines of multiples of a variable θ chosen so as to have its increment in a constant ratio to that of x and to vary from o to 2π between these given limits of x, the problem admits of but one solution; and Fourier has shown that the coefficients of the general terms of the series, *viz.*, $\sin m\theta$ and $\cos m\theta$ will be $\frac{1}{\pi}\int_0^{2\pi} f(x)\sin m\theta.d\theta$ and $\frac{1}{\pi}\int_0^{2\pi} f(x)\cos m\theta.d\theta$ respectively, for all integral values of m not zero, while the constant term or coefficient of $\cos o\theta$ is $\frac{1}{2\pi}\int_0^{2\pi} f(x).d\theta$.

If, however, it be agreed that the series shall represent the given function for a limited range only (less than 2π) of values of θ, an infinite number of solutions are possible; and the problem becomes determinate only when the value of the series for the remainder of the interval 2π of θ is specified. Advantage may be taken of this to impose additional conditions on the nature of the series by which the given function is to be represented.

If, for example, it be sufficient to find a series that will represent the function over the assigned range in values of x for values of θ between $\theta = o$ and $\theta = \pi$, no conditions being imposed as to the value of the series when θ lies between π and 2π, the value of the series in the latter range may be so chosen as to make the coefficients of either the sine terms or the cosine terms of the series equal to zero.

The first may be accomplished by making the series represent the ordinates of a curve with values of θ as abscissae, whose ordinates between $\theta = 0$ and $\theta = \pi$ are the corresponding values of $f(x)$ over the given range in the values of x, and which is continued between $\theta = \pi$ and $\theta = 2\pi$ by its mirror image in the ordinate at $\theta = \pi$. Representing by $\psi(x)$ the values of the ordinates throughout the whole range from $\theta = 0$ to $\theta = 2\pi$, the integral $\frac{1}{\pi}\int_0^{\pi} \psi(x) \sin m\theta . d\theta$ will then be equal in magnitude and opposite in sign to $\frac{1}{\pi}\int_{\pi}^{2\pi} \psi(x) \sin m\theta . d\theta$ and therefore $\frac{1}{\pi}\int^{2\pi} \psi(x) \sin m\theta . d\theta$ will be zero, while $\frac{1}{\pi}\int_0^{2\pi} \psi(x) \cos m\theta . d\theta$ will be equal to $\frac{2}{\pi}\int_0^{\pi} \psi(x) \cos m\theta . d\theta$, and the constant term $\frac{1}{2\pi}\int_0^{2\pi} \psi(x) . d\theta$ to $\frac{1}{\pi}\int_0^{\pi} \psi(x) . d\theta$; so that the series which represents $\psi(x)$ for all values of θ between $\theta = 0$ and $\theta = 2\pi$, and therefore *inter alia* represents $f(x)$ over the given range in x for values of θ between $\theta = 0$ and $\theta = \pi$, will consist of cosines only (besides the constant term). Thus the coefficient of the general term $\cos m\theta$ will be $\frac{2}{\pi}\int_0^{\pi} f(x) \cos m\theta . d\theta$ and the constant term is as just stated, or equivalently $\frac{1}{\pi}\int_0^{\pi} f(x) . d\theta$.

If on the other hand the ordinates of the curve represented by the series be equal to $f(x)$ for values of θ between $\theta = 0$ and $\theta = \pi$, while the part of the curve between $\theta = \pi$ and $\theta = 2\pi$ is formed from the first part by revolution through 180° round the point $\theta = \pi$ on the axis of abscissae, the cosine terms disappear and the coefficient of the general term $\sin m\theta$ is $\frac{2}{\pi}\int_0^{\pi} f(x) \sin m\theta . d\theta$, there being here no constant term.

These "cosine series" and "sine series" are discussed in all works dealing with Fourier series; the textbooks with which we are familiar, however, do not point out that still further conditions may be imposed on the nature of the series if the range of values of θ through which it is to represent $f(x)$ be still further restricted. Such conditions are met with in practice; for instance, in order to obtain Eq. (54*e*) Eq. (72) and Eq. (79) of the present paper (see also Eq. 11) it was necessary to find a series of *sines of odd multiples* of $\theta = \pi x/2l$ which would represent a given function of x between the limits $\theta = 0$ and $\theta = \pi/2$. This condition is complied with if the series be constructed to represent the ordinates of a curve, whose ordinates between $\theta = 0$ and $\theta = \pi/2$ are equal to $f(x)$, and which is continued in the second quadrant by its mirror image in the vertical through the point $\theta = \pi/2$, while the second half is formed from the first by rotation through 180° around the centre $\theta = \pi$ on the axis of abscissae. For such a case $\int_0^{2\pi} \psi(x).\cos m\theta.d\theta = 0$ as stated above, while $\frac{1}{\pi}\int_0^{2\pi} \psi(x) \sin m\theta.d\theta$ is zero when $m = 2n$, and equals $\frac{4}{\pi}\int_0^{\frac{\pi}{2}} \psi(x).\sin m\theta.d\theta$ or $\frac{4}{\pi}\int_0^{\frac{\pi}{2}} f(x).\sin m\theta.d\theta$ when $m = 2n - 1$. So that the series which represents $f(x)$ for all values of θ between $\theta = 0$ and $\theta = \frac{\pi}{2}$, will consist of sines of odd multiples only of θ and the coefficient of the general term, *viz.*, $\sin(2n - 1)\theta$ will be $\frac{4}{\pi}\int_0^{\frac{\pi}{2}} f(x).\sin(2n - 1)\theta.d\theta$.

Similarly, the general term of the series which represents $f(x)$ for values of θ between $\theta = 0$ and $\theta = \frac{\pi}{2}$ and which

consists of cosines of odd multiples only of θ, is

$$\frac{4}{\pi}\cos(2n-1)\theta.\int_0^{\frac{\pi}{2}} f(x).\cos(2n-1)\theta.d\theta.$$

The extension to the other three quadrants which this series is made to define is obtained as follows: revolve the curve in the first quadrant about the point $\theta = \frac{\pi}{2}$ on the axis of abscissae through 180° to define the second quadrant, and then for the second half take the mirror image of the first two quadrants in the ordinate at $\theta = \pi$.

It is to be noted, however, that these extensions are introduced merely for the purpose of explanation, and, as the results above show, do not need to be represented graphically or introduced into the formulae.

Although values different from zero may be obtained from the above formulae for the coefficients of terms which are not to appear in the series, no use is to be made of such values, as the formula is not valid for any such purpose. Similarly in the last case for which the formula is given (cosines of odd multiples) there is no constant term, whatever be the mean value of $f(x)$ over the given range in x.

University of Toronto,
July, 1910

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The following contractions are employed throughout:

$$a = \pi^2 k/4l^2 \qquad \mu = \sqrt{\frac{\omega}{2k}}$$

$$b = \sqrt{\frac{K}{k}} \qquad \sum = \sum_{n=1}^{\infty}$$

$$C = G/k \qquad \xi = l - x$$

$$g = \pi/2l \qquad \phi = K + m^2 a$$

$$m = 2n - 1$$

Equations presenting different algebraical forms of the same relations are given the same number, but distinguished by the use of the letters a, b, c, etc.

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No. 93: THE BEHAVIOUR OF COPPER ANODES IN CHLORIDE SOLUTIONS, BY SAUL DUSHMAN

(REPRINTED FROM THE JOURNAL OF PHYSICAL CHEMISTRY, VOL. XIV)

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THE BEHAVIOR OF COPPER ANODES IN CHLORIDE SOLUTIONS

BY SAUL DUSHMAN

INTRODUCTION

In connection with some experiments on the electrolytic etching of copper alloys, my attention was drawn to the behavior of pure copper anodes in solutions of chlorides. I found that it was possible to make the copper dissolve wholly as cupric or wholly as cuprous salt or as a mixture of these in any desired proportions, by varying the current density or the concentration of chloride in solution. The observation that increasing the concentration of chloride increases the proportion of cuprous salt formed,[1] suggested that there may be equilibrium at the surface of the electrode between metallic copper and the cuprous and cupric salts in solution. The effect on the proportion of cuprous salt consequent on lowering the current density,[2] stirring the solution,[3] or increasing the rate of circulation,[4] may also be explained in the same manner; for all these processes tend to lessen the difference in composition between the solution at the electrode and that in the body of the electrolyte, *i. e.*, they raise the concentration of the chloride and diminish that of the dissolved copper salts at the surface of the anode,[5] and thus increase the proportion of cuprous salt formed.[6]

The assumption of equilibrium at the electrode is not new,[7] it has been put forward to explain the behavior of gold anodes

[1] See experiments 1-6 Table I.

[2] See experiments 10-12 Table II.

[3] Compare experiments 7 and 8 5 and 9 Table I.

[4] See experiments 13-16 Table II.

[5] See abstract of preliminary work, Trans. Roy. Soc. Can. Sec. III, p. 26 (1907).

[6] A brief account of these experiments was given at the meeting of the American Chemical Society at Toronto, June 1907.

[7] Foerster: Elektrochemie wässr. Lösungen, p. 212, etc.

TABLE I

Beaker experiments. Stationary electrodes. Hydrochloric acid solutions. Area of electrodes = 2.5 × 2.5 cms

No.	Concentration	Current density (Amps/cm²) gram	Total copper dissolved gram	Percent cupric	Percent cuprous	Stirring
1	N/1	0.02286	0.760	0	100	Yes
2	N/10	0.02286	0.429	87	13	Yes
3	N/40	0.02286	0.341	100	0	Yes
4	N/1	0.00514	0.602	0	100	Yes
5	N/2	0.00514	0.508	30	70	Yes
6	N/4	0.00514	0.372	77	23	Yes
7	N/1	0.00416	0.609	0	100	Yes
8	N/1	0.00416	0.422	53	47	No
9	N/2	0.00514	0.360	80	20	No

TABLE II

Beaker experiments. Circulating electrolyte. Rotating anode. Solution N/10 HCl. Duration of each experiment, 30 minutes

	Volume circulated liters	Current density (Amp./cm²)	Total copper dissolved	Percent cupric	Percent cuprous
10	10.6	0.016	0.2392	16.0	84.0
11	11.0	0.107	0.9403	94.0	6.0
12	10.0	0.300	2.7000	100.0	0.0
13	15.7	0.109	1.0107	88.2	11.8
14	33.5	0.109	1.0523	83.7	16.3
15	39.0	0.109	1.0910	79.3	20.7
16	48.4	0.109	1.1354	74.4	25.6

in chloride solutions[1] of copper anodes in sulphate solutions[2] and of anodes of tin, antimony and bismuth in a number of different electrolytes.[3] *In no case however have quantitative measurements been made by which the hypothesis of equilib-*

[1] Wohlwill: Zeit. Elektrochemie, **4**, 405 (1898).

[2] Foerster and Seidel: Zeit. anorg. Chem., **14**, 106 (1897).

[3] K. Elbs and H. Thummel: Zeit. Elektrochemie, **10**, 364 (1904); K. Elbs and J. Forssell: Ibid., **8**, 760 (1902); K. Elbs: Ibid., **8**, 512 (1902); K. Elbs and F. Fischer: Ibid., **7**, 343 (1900).

rium could be controlled, and the object of the experiments described in this paper is to supply this deficiency.[1]

My electrolyses were consequently carried out under conditions that allowed the concentrations of the various constituents of the solution at the anode to be ascertained; and the concentrations so determined were compared with the requirements of the Mass Law.

APPARATUS

In designing the apparatus it was necessary first to provide a uniform field, so that the current density might be the same at every part of the anode, second, to exclude air as far as possible, so that there might be no "chemical" solution of the anode, and third, to keep the copper salts from reaching the cathode, so that the composition of the electrolyte might depend only on the anode reactions. Arrangements had also to be made for varying the composition and rate of circulation of the electrolyte, as well as the rate of rotation of the anode. The current was determined by an ammeter and a copper (or silver) voltameter in the circuit.

Fig. 1. shows the apparatus finally used.[2] It consisted of two porous cylinders P_1 and P_2 cemented to the cylinder E and the bottom piece F which were of hard rubber, and a rotating copper anode A making contact by means of a wire W with a shaft S and holder H. A plug of hard rubber T was provided with a threaded perforation so that it could be tightened against the copper tube as shown in the diagram. The tube could therefore be taken off the shaft and weighed. Rubber rings *r* and pieces of tubing *b* prevented any electrolyte entering the tube. The access of air to the solution passing over the anode was prevented by means of hydro-

[1] NOTE.—After these experiments were well under way, an abstract of a paper originally published in Russian appeared in Chem. Cent. **2**, 1243 (1907) in which the hypothesis is advanced that equilibrium exists at the surface of copper anodes in chloride solutions and of mercury anodes in nitrate solution. No quantitative measurements however are given except in the case of mercury in solution of potassium nitrate.

[2] A description of an earlier form of apparatus will be found in Trans. Am. Electrochem. Soc., **13**, 314 (1908).

chloric acid (of the same strength as that circulating through the cell) which was contained in the circular groove R in which rotated the hard rubber cover C. The electrolyte entering B passed over the anode, through the glass tube K

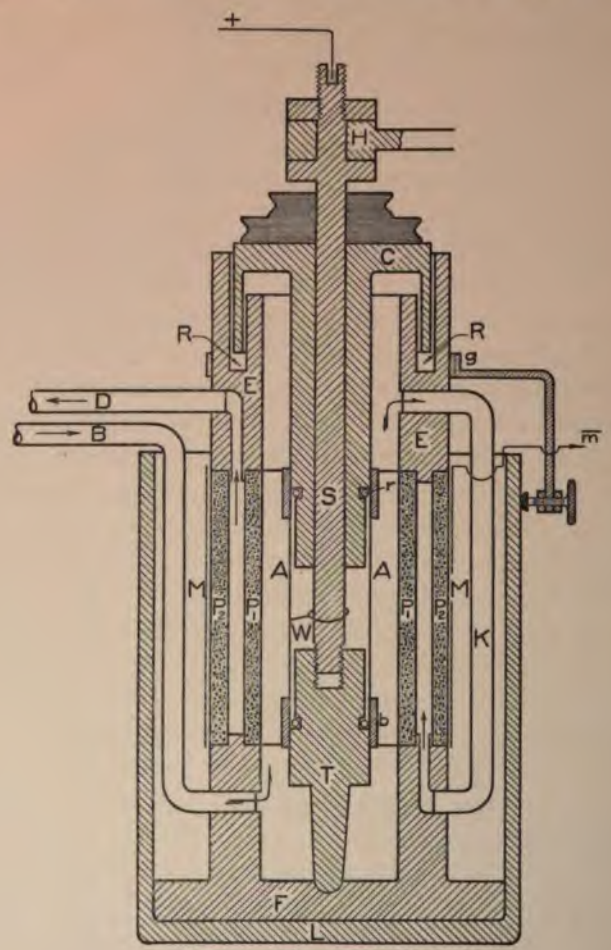

Fig. 1

into the compartment between the two porous cylinders and left it by means of the exit tube D. The cathode consisted of a platinum gauze M wrapped around the outside of P. The different parts of the apparatus were cemented together

with a cement consisting of one part rubber and three parts resin. Three rubber-tipped screw clamps *k* attached to a brass ring g and clamped to the glass jar L (which contained the cathode solution) prevented any lateral motion of the cell when the anode was set rotating.

The stock solution, contained in a tubular 12-liter bottle, was freed from air by exhaustion (a mercury manometer was used to indicate the degree of exhaustion), and was then saturated with purified carbon dioxide gas. During the electrolysis, this solution was kept under an atmosphere of the gas and furthermore on its way from the tubulus into the inlet tube B of the cell it was joined by a stream of carbon dioxide gas; in this manner the cell could be filled with the gas before electrolysis, and oxidation of cuprous salt formed during the experiment was reduced to a minimum. After circulating through the cell once, the electrolyte passed into a measuring cylinder and was then discarded.

With these precautions to exclude air, the loss of weight of the anode when rotated (without current) was extremely small as is evident from the following data:

Hydrochloric acid (1.84×10^{-2} N) was circulated through the cell for one hour. In the first two experiments air-saturated solution was used, in the third, solution which had been completely freed from air by exhaustion and saturated with carbon dioxide gas, and in the fourth, a mixture of equal volumes of air-saturated and carbonated solutions.

No.	V	L	10^3L/V
1	3.2	0.0148	4.6
2	2.4	0.0085	3.5
3	2.7	0.0008	0.3
4	2.2	0.0050	2.3

Under V is given the number of liters of solution circulated, and under L, the loss in weight of the copper tube. It appears from these results that the rate of solution of the copper in hydrochloric acid solutions containing air is approximately proportional to the concentration of oxygen.

In another experiment with 5×10^{-3} N acid, 6.0 liters solution (air-free) were circulated in an interval of 7 hours and only 0.0028 gram was dissolved,[1] corresponding to 0.45×10^{-3} gram per liter.

THE CONCENTRATIONS IN THE BODY OF THE SOLUTION

To find the quantity of cupric and cuprous salts, respectively, formed during an experiment, the total copper dissolved in an experiment (P grams) was compared with the copper (Q) or silver, deposited in a voltameter in the circuit. Then 2(P-Q) gms is the weight of copper dissolved as cuprous salt, and 2Q-P is the weight of copper as cupric.

The concentrations of the cupric and cuprous salts in the electrolyte, expressed in *mols per litre*,[2] may therefore be represented by

$$[\text{Cupric}] = \frac{2Q - P}{63.6\,V}$$

$$[\text{Cuprous}] = \frac{2(P - Q)}{63.6\,V},$$

where V is the total volume of the electrolyte passed through the cell (in liters).[3] In the calculations which follow, it is assumed that the cupric salt is totally dissociated in solution into the ions $\overset{++}{Cu}$ and $\overset{-}{Cl}$, so that

$$[\overset{++}{Cu}] = \frac{2Q - P}{63.6\,V}. \qquad \text{(I)}$$

The cuprous salt on the other hand is assumed to exist in two forms,[4] $\overset{+}{Cu}$ and $\overset{-}{CuCl_2}$, so that

[1] As the anode itself weighed about 75 g. these small losses could not be determined with accuracy.

[2] By one mol cuprous or cupric salt is understood the quantity containing 63.6 g. copper. The concentrations in the body of the solution are distinguished by square brackets.

[3] This assumes that the solution passing through the cell arrives at a stationary composition in an interval of time which is very small compared to the total duration of the experiment.

[4] Bodländer and Storbeck: Zeit. anorg. Chem., 31, 1 (1902). In a paper which will be published shortly, these equilibrium experiments will be discussed more fully.

$$[\overset{+}{Cu}] + [\overset{-}{CuCl_2}] = \frac{2(P-Q)}{63.6\,V}. \qquad \text{(II)}$$

It was thought by Bodländer and Storbeck that the ratio $\overset{+}{Cu}/\overset{-}{CuCl_2}$ would be given by

$$(\overset{+}{Cu}) \times (\overset{-}{Cl})^2 = K'(\overset{-}{CuCl_2}) \qquad \text{(III)}$$

corresponding to the chemical equation

$$\overset{+}{Cu} + 2\overset{-}{Cl} \rightleftarrows \overset{-}{CuCl_2}.$$

Careful examination of their results, and some work of my own, however, shows that the "constant," K′, varies from 1.22×10^4 to 6.13×10^4 in different experiments. I have consequently thought it best to plot

$$y = \frac{(\overset{+}{Cu})}{(\overset{+}{Cu}) + (\overset{-}{CuCl_2})}$$

from their experiments (Table III) with different values of $(\overset{-}{Cl})$ and to use the graph (Fig. 2) instead of equation (III).

TABLE III

Solubility determinations of cuprous chloride in potassium chloride solutions (Bodländer and Storbeck)

$\overset{-}{Cl}$	$(\overset{+}{Cu})$	$(\overset{+}{Cu}) + (\overset{-}{CuCl_2})$	y
4.55	0.398	0.646	0.616
4.38	0.246	0.484	(0.508)[1]
4.65	0.336	0.589	0.570
5.03	0.263	0.534	0.492
5.28	0.178	0.460	0.387
6.37	0.175	0.514	0.340
9.97	0.233	0.761	0.306
13.76	0.282	1.022	0.276
17.80	0.205	1.122	0.183

(N. B. All the concentrations in this table are expressed in millimols per liter.)

[1] This determination was not used in plotting the curve. In the graph (see p. 906) the "chlorion" is in the same units as those used in the above table.

THE CONCENTRATIONS AT THE ELECTRODE

Immediately at the surface of the anode, the concentrations of the copper salts are greater than those in the body of the solution, the difference depending on the rate at which the copper is being dissolved. If it be assumed that the copper salt formed must diffuse through an adherent liquid film of constant thickness, l cms., and that the "diffusion-constant," k (in cm^2/sec.) is independent of the concentration, then the difference in concentration due to the diffusion is given by

$$\frac{10^3 l}{k} \times \frac{(\text{Mols salt formed per second})}{(\text{Area of electrode in cms}^2)}.^{1}$$

These assumptions may be made in the case of the copper salts and hydrochloric acid, so that if the concentrations at the anode be distinguished from those in the body of the solution by the use of curved brackets, { },

$$\{\overset{+}{Cu}\} + \{\overset{-}{CuCl_2}\} = \frac{2(P-Q)}{63.6}\left(\frac{1}{V} + \frac{10^3 l}{k_1 A t}\right) \qquad \text{(IV)}$$

$$\{\overset{++}{Cu}\} = \frac{(2Q-P)}{63.6}\left(\frac{1}{V} + \frac{10^3 l}{k_2 A t}\right) \qquad \text{(V)}$$

where k_1 is the diffusion-constant of cuprous salt, k_2 that of cupric, A, the area of the electrode-surface (in cms^2) and t, the duration of the electrolysis in seconds.

Values of $\{\overset{-}{Cl}\}$, the concentration of chlor ion at the electrode, may be calculated from the equation,

$$\frac{4(P-Q)(1-y)}{63.6\,t} = \frac{k_3 A}{10^3 l}([\overset{-}{Cl}] - \{\overset{-}{Cl}\}) + \frac{HQ}{31.8\,t}, \qquad \text{(VI)}^{2}$$

where the term on the left denotes twice the number of mols $\overset{-}{CuCl_2}$ formed per second at the electrode; the first term on the right, the number of mols $\overset{-}{Cl}$ reaching the anode per second by diffusion; and the last term, the number of mols

[1] Since k, l, and the area of the electrode are measured in cm-units, the factor 10^3 is necessary to convert the concentration difference into *mols per liter*.

[2] k_3 is the diffusion constant of hydrochloric acid and H, the transport number of chlorine in the solution.

$\overline{Cl}$ transported electrolytically to the anode per second. Thus,

$$\{\overline{Cl}\} = [\overline{Cl}] - \frac{10^3 l[2(P-Q)(1-y)-HQ]}{31.8\, k_3 A t}. \qquad \text{(VII)}$$

As in my experiments $\{\overline{Cl}\}$ and $[\overline{Cl}]$ do not differ greatly, an approximate value of

$$y = \frac{[\overset{+}{Cu}]}{[\overset{+}{Cu}] + [\overline{CuCl_2}]}$$

calculated on the assumption that $\{\overline{Cl}\}$ and $[\overline{Cl}]$ are equal, is sufficiently accurate for the purpose of equation (VII).

Using the value of $\{\overline{Cl}\}$ calculated according to this equation, the ratio,

$$Y = \frac{\{\overset{+}{Cu}\}}{\{\overset{+}{Cu}\} + \{\overline{CuCl_2}\}} \qquad \text{(VIII)}$$

was determined from the graph.

APPLICATION OF THE MASS LAW

Eliminating $\{\overset{+}{Cu}\} + \{\overline{CuCl_2}\}$ from (IV) and (VIII), and comparing the result with (V), there follows,

$$\frac{\{\overset{++}{Cu}\}}{\{\overset{+}{Cu}\}^2} = \frac{\frac{(2Q-P)}{63.6}\left(\frac{1}{V} + \frac{10^3 l}{k_2 A t}\right)}{\left(\frac{2Y(P-Q)}{63.6}\left(\frac{1}{V} + \frac{10^3 l}{k_1 A t}\right)\right)^2}. \qquad \text{(IX)}$$

According to the Mass Law applied to the reaction,

$$\overset{\circ}{Cu} + \overset{++}{Cu} \rightleftharpoons 2\overset{+}{Cu}$$

the expression (IX), in which nothing but experimentally determinable quantities appear, ought to be a constant. In the tables which follow I have denoted it by K.

Of the quantities involved in (IX), Q, P, V, A, t, and Y

have already been discussed; there remain only the two ratios l/k_1 and l/k_2. These were determined directly as described in the following sections; in order to check the results, l itself was determined (page 899) and the resulting values of k_1 and k_2, were compared with those deducible from theoretical considerations.

In calculating Y, two other constants were employed, *viz.*, H and k_3. Of these H = 0.167 is taken from the recent measurements of Noyes and Kato,[1] which are in accord with those of Jahn.[2] The diffusion constant of hydrochloric acid, $k_3 = 2.67 \times 10^{-5}$ is obtained from the work of Öholm[3] by averaging his results from 0.01 and 0.02 normal acid and converting into the units (cm^2/sec.) of the present paper.

Determination of l/k_2

The following method for the determination of this constant suggested itself during the course of the investigation.

Solutions containing hydrochloric acid and copper chloride in known quantities were passed through the cell of the apparatus shown in Fig. 1, while the copper cylinder A was revolving without current. The loss in weight (W grams) of the copper was determined while V liters of the solution passed through the cell in the interval t seconds.

Under these circumstances the cupric chloride at the immediate surface of the copper is reduced almost quantitatively to cuprous salt.[4] Assuming that the rate of reduction of the cupric chloride is very much greater than the rate at which it is renewed by diffusion,[5] it follows that the concentration of cupric chloride at the immediate surface of the copper must be practically zero, and consequently that the

[1] A. A. Noyes and Y. Kato: Zeit. phys. Chem., **62**, 420 (1908).

[2] H. Jahn: Zeit. phys. Chem., **58**, 641 (1907).

[3] L. W. Öholm: Zeit. phys. Chem., **50**, 309 (1904).

[4] Bodländer and Storbeck: Zeit. anorg. Chem., **31**, 1 (1902).

[5] Bodländer and Storbeck's experiments: loc. cit. show that the reduction is very rapid.

rate of flow of cupric chloride through the diffusion-film is equal to its rate of reduction. That is,

$$\frac{W}{63.6\,t} = \frac{k_2 A}{10^3 l}\,[\overset{++}{Cu}] \qquad (X)$$

where $[\overset{++}{Cu}]$ denotes the concentration of cupric chloride in the body of the solution (in mols per liter). The following table gives the experimental data, together with the values of l/k_2 calculated by means of (X).

TABLE IV[1]

Temp. = 18°, A = 47, rate of rotation = 1600 per minute

No.	[HCl]	$[\overset{++}{Cu}]$	W	t_0	V	l/k_2
1	0.0930	0.0497	0.2220	3600	2.2	2350
2	0.0920	0.0484	0.3496	5400	3.5	2220
3	0.0964	0.0072	0.1497	3600	3.1	500
4	0.0966	0.0059	0.1697	4800	3.4	495
5	0.0933	0.0035	0.1565	5400	3.25	360

These measurements show that while l/k_2 increases very rapidly with the dilution in concentrated solution, it tends to attain a constant value for extremely dilute solutions. As the concentrations of cupric chloride obtained in the electrolytic experiments were all less that used in experiment 5 of the above table, the assumption may be made that l/k_2 is constant for these concentrations, and for reasons which will be discussed subsequently (in the section on diffusion constants) the value $l/k_2 = 333$ has heen used in the calculations which follow.

Determination of l/k_1

The solubility experiments described in the previous section were also used for the determination of l/k_1. Assuming that at the immediate surface of the copper the solution is saturated with cuprous chloride, values of {*Total Cuprous*}

[1] In experiments 3, 4, and 5, the quantity of cupric salt reduced to cuprous has been allowed for when calculating $[\overset{++}{Cu}]$.

may be calculated from the solubility measurements of Bodländer and Storbeck[1] and inserted in the equation,

$$\frac{W}{63.6\,t} = \tfrac{1}{2} \times \frac{k_1 A}{10^3 l}(\{\text{Total Cuprous}\} - [\text{Total Cuprous}]), \quad \text{(XI)}$$

whence values of l/k_1 may be calculated. In this equation the expressions in curved brackets { } and square brackets [] denote concentrations (in mols per liter) at the electrode and in the solution respectively, and W, t, and A have the same values as in Table IV. The values of [*Total Cuprous*] have been calculated by the relation,

$$[\text{Total Cuprous}] = \frac{2\,W}{63.6\,V}. \quad \text{(XII)}$$

TABLE V

No.	{Total Chlorine}	{Total Cuprous}	[Total Cuprous]	l/k_1
1	0.1890	0.00850	0.00318	(125.0)
2	0.1890	0.00850	0.00313	122.6
3	0.1107	0.00500	0.00152	125.0
4	0.1099	0.00495	0.00157	142.9
5	0.1028	0.00463	0.00152	160.4
			Average =	138.0

In the subsequent calculations of this paper, the value, $l/k_1 = 138$ has consequently been used.

While the values of l/k_1 and of l/k_2 determined in the above manner give sufficient information for the purpose of equation (IX), it nevertheless seemed desirable to obtain independent values of l, k_1 and k_2, so that the latter might be compared with the values deducible from the mobilities by means of Nernst's formula. These determinations, which

[1] Loc. cit. For the concentrations of chlorine used in these solubility experiments,

$$\{\text{Total Cuprous}\} = \frac{\{\text{Total Chlorine}\}}{22.2}$$

are detailed in the following paragraphs resulted in the adoption of a valve of l/k_2 slightly lower than the lowest found in Table IV.

Determination of l the Thickness of the Film

A. From Experiments with Oxalic Acid

Ackerberg,[1] using a platinized platinum anode, found that the rate of oxidation of oxalic acid dissolved in large excess of sulphuric acid (20 percent conc. H_2SO_4 by volume), may be represented by the equation.

$$\frac{dx}{dt} = \frac{k(B - x)}{V}, \qquad \text{(XIII)}$$

when high current densities are used and the electrolyte is stirred. In this equation, dx/dt gives the number of equivalents oxalic acid oxidized per second and B is the number of equivalents oxalic acid in V liters of the solution at $t = 0$.

Nernst and Brunner[2] and Lorenz[3] have shown that this result is in accord with the hypothesis of diffusion towards the electrode, according to which the number of equivalents oxidized per second is equal to that diffusing to the electrode in the same time. That is, for current densities greater than the limiting value, k (in equation XIII) $= k_4\ A/10^3 l$, where k_4 is the diffusion constant of oxalic acid (in cm^2/sec.), A, the area of the electrode (in cms^2) and l the thickness of the film (in cms).

Making this substitution in (XIII) and integrating, we find.

$$\frac{k_4 A}{10^3 l V} = \frac{2.3}{t_2 - t_1}\left(\log_{10}\frac{B - x_1}{V} - \log_{10}\frac{B - x_2}{V}\right), \qquad \text{(XIII}a\text{)}$$

where x_1 and x_2 are the number of equivalents oxalic acid oxidized at the end of intervals t_1 and t_2 respectively.

From a knowledge of k_4, A, and the rate of oxidation of a solution of oxalic acid in maximum conductivity sulphuric acid, it is therefore possible to determine l. The value of

[1] Ackerberg: Zeit. anorg. Chem., **31**, 161 (1902).

[2] Zeit. phys. Chem., **47**, 52, 56 (1904).

[3] Electrochemie, **1905**, pp. 239–44.

k_4 was calculated from the mobility of $\overline{C_2O_4}$ by applying Nernst's equation[1] as modified by Abegg and Bose,[2]

$$k_4 = \frac{u}{2} \times \frac{0.04485}{86400}. \qquad \text{(XIV)}$$

Since $u = 39$ for decinormal oxalic acid, therefore $k_4 = 1.01 \times 10^{-5}$.

In order to obtain a value for l under conditions as nearly similar as possible to those obtaining in the electrolytic experiments with hydrochloric acid solution, the same shaft and stirring arrangement were used as that described on page 888. The copper tube, however, was covered with platinum foil and platinized according to the directions of Kohlrausch and Holborn,[3] and the cell of Fig. 1 was replaced by a porous pot of about 750 cc capacity surrounded by a cylindrical cathode of lead. The electrolyte for the anode compartment contained about 3.5 g crystallized oxalic acid and 200 cc concentrated sulphuric acid per liter, that for the cathode compartment contained the same amount of sulphuric but no oxalic acid.

During the electrolysis, 10 cc samples of the anode solution were pipetted out at definite intervals and titrated against standard permanganate.

TABLE VI

Rate of oxidation of oxalic acid

No.	Current	t	$t_2 - t_1$	$\frac{B-x}{V}$	V	l
–	—	0	—	0.0592	—	—
1	0.45	3600	3600	0.0454	0.63	10.1×10^{-3}
2	0.95	5400	1800	0.0392	0.62	9.3×10^{-3}
3	1.35	6300	900	0.0362	0.61	9.1×10^{-3}
					Average	9.5×10^{-3}

[1] Nernst: Theoret. Chem., III Auflage, p. 361.

[2] Zeit. phys. Chem., 30, 545 (1899).

[3] The electrode was platinized while rotating, thus securing a smooth eposit.

B. From Experiments with Copper Sulphate

In the electrolysis of a solution containing both copper sulphate and sulphuric acid, the concentration of the copper at the immediate surface of the cathode is lowered as the current density is increased until a value of the latter is attained at which the concentration is practically zero. Increasing the current density still more causes hydrogen to be liberated along with the copper, which is indicated by an abrupt rise in voltage over the cell.

Just before this point is reached the amount of copper removed from the electrolyte is equal to that carried to the electrode by diffusion, since in the presence of sulphuric acid migration of the copper may be neglected. Thus,

$$\frac{I' \times 31.8}{96540} = \frac{k_5 A}{10^3 l} [CuSO_4], \qquad \text{(XV)}$$

where I'/A is the current density at which hydrogen first appears, k_5 is the diffusion constant (in cm^2/sec.) of copper sulphate and the expression in square brackets denotes concentration in grams per liter.

Working with the apparatus described on p. 888 (where $A = 47$) I found $I' = 0.069$ at 18° C and 1600 revolutions per minute (see Tables VII and VIII). The diffusion constant of copper sulphate is given by Wiedeburg[1] as $0.4479 \times 10^{-5} \times (1 - 3.467c)$ where c denotes the concentration in grams of copper per cm^3. Sand[2] found the same value for solutions of copper sulphate in sulphuric acid (0.0881 to 0.1804 normal). For the concentration of copper used in the experiments recorded in Tables VII and VIII $k_5 = 0.44 \times 10^{-5}$. Hence using $I' = 0.069$, $l = 4 \times 10^{-3}$.

[1] Wied. Ann., 41, 675 (1890).
[2] Phil. Mag. [6], 1, 45 (1901).

TABLE VII

Determination of limiting current

Experiment I		Experiment II	
Voltage	Current	Voltage	Current
0.125	0.021	0.125	0.020
0.160	0.025	0.160	0.026
0.200	0.035	0.190	0.030
0.280	0.057	0.240	0.040
0.300	0.067	0.320	0.067
0.340	0.110	0.380	0.120
—	I′ = 0.067	—	I′ = 0.068

TABLE VIII

Determination of limiting current

While these readings were taken, the electrolyte was allowed to flow over the cathode as in the experiments of Tables X and XI.

Experiment III		Experiment IV	
Voltage	Current	Voltage	Current
0.17	0.022	0.18	0.020
0.20	0.030	0.20	0.025
0.25	0.040	0.26	0.033
0.34	0.065	0.32	0.050
0.38	0.110	0.37	0.067
0.40	0.115	0.42	0.110
0.40	0.122	0.48	0.140
—	I′ = 0.070	—	I′ = 0.070

The value of l obtained by the oxalic method is higher than that obtained by the second. This is probably due to the value selected for the diffusion-constant of oxalic acid. The diffusion constant for copper calculated from the mobility (at the concentration used in the above experiments) is 0.7×10^{-5} while the direct experiments quoted above gave 0.44×10^{-5}. If the calculated value of the diffusion constant of oxalic acid be reduced in the same proportion, l as calculated by the first method becomes 6×10^{-3}.

Diffusion Constants of Cupric and Cuprous Chlorides

Although the diffusion constant for copper sulphate has been determined for concentrated aqueous solutions and for solutions containing sulphuric acid (see above p. 899) there are no data for the diffusion constant of copper in very dilute solutions of cupric chloride containing hydrochloric acid. From the values of l/k_2 in Table IV and the result $l = 4 \times 10^{-3}$, the following numbers are calculated for k_2.

TABLE IX

No	$\{\overset{++}{Cu}\}$	k_2
1	0.0479	0.17×10^{-5}
2	0.0485	0.18×10^{-5}
3	0.0072	0.80×10^{-5}
4	0.0059	0.81×10^{-5}
5	0.0035	1.11×10^{-5}

These numbers show that k_2 increases with the dilution. Using the value 50.5 for the mobility of $\overset{++}{Cu}$ at infinite dilution,[1] k_2 may be calculated from the equation

$$k_2 = \frac{u}{2} \times \frac{0.04485}{86400} \qquad \text{(XIV)}$$

which gives $k_2 = 1.30 \times 10^{-5}$. As mentioned previously the concentrations of cupric chloride obtained in the electrolytic experiments were all less than that of the most dilute solution of Table IX. Accordingly the average of 1.30×10^{-5} and 1.11×10^{-5}, that is 1.2×10^{-5}, has been taken as the value of k_2 in the electrolytic experiments. Hence $l/k_2 = 333$.

The diffusion constant of cuprous chloride dissolved in hydrochloric acid may be calculated similarly from the value

[1] The mobility of $\overset{++}{Cu}$ for binary electrolytes at infinite dilution is given by Kohlrausch and Holborn as 50. By analogy with $\overset{++}{Zn}$ the value of the mobility of $\overset{++}{Cu}$ in $CuCl_2$ may be taken as about 50.5.

of $l/k_1 = 138$, and is found to be 2.9×10^{-5}. Although this value is noticeably higher than any that might be deduced from the mobility of $\overline{Cl}$ or from the analogy of $Cu\overline{Cl}_2$ with other complex ions, yet it seems unlikely that the value of k_1 can be less than 2.9×10^{-5} (that is, assuming $l = 4 \times 10^{-3}$) for in that case it would be necessary to assume that the solution at the immediate surface of the copper is supersaturated with respect to cuprous chloride.[1]

DISCUSSION OF RESULTS

Table X gives, together with the experimental data, the values of K calculated according to equation IX. The numbers so found vary between 0.5×10^4 and 3.5×10^4. Bodländer and Storbeck's work in which copper powder and cuprous chloride were shaken with solutions of potassium chloride gives $K = 1.5 \times 10^4$. Considering the wholly different nature of the two series of experiments this agreement must be regarded as a remarkable confirmation of the theory of the electrolysis set forth in the introduction.

As, however, the values of K calculated according to equation IX, are largely and unequally affected by the unavoidable error of experiment, I have thought that a recalculation of the anode losses, assuming the constant $K = 1.5 \times 10^4$ would furnish a more satisfactory test of the validity of the theory.

In making this recalculation, $K = 1.5 \times 10^4$; $l/k_1 = 1.38$ and $l/k_2 = 3.33$ were substituted in equation IX, which then becomes,

$$\frac{\frac{(2Q-P)}{63.6}\left(\frac{1}{V} + \frac{3.33}{At}10^5\right)}{\left[\frac{2y(P-Q)}{63.6}\left(\frac{1}{V} + \frac{1.38}{At}10^5\right)\right]^2} = 1.5 \times 10^{-4}. \qquad \text{(XVI)}$$

For each experiment the proper values of Q, t, A and V, were then introduced and a value of y taken from the graph

[1] In some of the experiments of Table IV, the copper cylinder became covered with a white coating of cuprous chloride.

on the assumption that $\{\overline{Cl}\} = [\overline{Cl}]$. The resulting quadratic equation in (P—Q) was solved, giving the value of P entered under "*P calc.*" next to the observed values.

In most of the experiments the observed and calculated anode losses agree to within 3 to 4 milligrams, although the conditions were varied to quite a large extent. Thus, the concentration of hydrochloric acid was varied from 4.65×10^{-3} to 16.15×10^{-3} normal, the current from 0.013 to 0.051 ampere, the anode area from 18 to 47 cm,^{2} and the rate of circulation of the electrolyte from 0.242 to 2.361 cm^3 per second.

The greatest discrepancies between "*P calc.*" and "*P obs.*" are to be found in those experiments whose duration was rather long, *e. g.*, Nos. 28, 35, 38, 43 and 57. This was undoubtedly due to oxidation of cuprous salt by air, which in spite of all precautions, must have entered the cell. A similar reason is to be assigned for the high anode losses observed with small currents. From the table it is seen that the differences in concentration of the cupric and cuprous salts at the electrode and in solution were very considerable, so that the corrections for diffusion were in many cases the main items in the calculation of K. Consequently any errors in measuring A or V/t, or any slight variation in the rate of stirring during the experiment affected the calculated value of K considerably. The fact that for low values of $\overline{Cl}$, the anode losses calculated are uniformly greater than those observed (see experiments 7, 8, 12–16) must be ascribed to an error in the determination of y, which is quite probable in view of the form which the graph for it assumes for values of $\overline{Cl}$ less than 5.5×10^{-3} (see Fig. 2).

As a further test of the validity of the theory I have also performed four experiments (see Table XI) in which a solution, approximately 9.0×10^{-3} normal in hydrochloric acid aud 0.171×10^{-3} molar in cupric chloride was used as elec-

Table X

Room temperature; 1600 revs. per minute

No.	$10^3 \times$ [Cl]	I (Amp.)	P obs.	P calc.	Q	V	t	$10^4 \times V/t$
1	11.60	0.0505	0.0752	0.0802	0.0599	2.99	3600	8.31
2	8.22	0.0498	0.1422	0.1460	0.1110	3.28	7200	4.56
3	13.50	0.0470	0.1438	0.1528	0.1113	5.80	7200	8.06
4	8.22	0.0436	0.1173	0.1174	0.0900	2.58	6000	4.30
5	9.18	0.0385	0.0613	0.0631	0.0456	6.43	3600	17.86
6	8.75	0.0250	0.0778	0.0850	0.0576	9.84	7200	13.68
7	5.29	0.0231	0.0402	0.0430	0.0297	2.53	3600	7.03
8	5.55	0.0253	0.0406	0.0439	0.0299	2.54	3600	7.05
9	12.60	0.0454	0.1469	0.1464	0.1080	3.45	7200	4.79
10	6.61	0.0246	0.0391	0.0404	0.0489	6.20	3600	17.22
11	4.65	0.0249	0.0691	0.0645	0.0502	2.32	6120	3.78
12	5.30	0.0250	0.1223	0.1278	0.0888	7.22	10800	6.68
13	5.27	0.0246	0.0407	0.0426	0.0293	2.47	3600	6.86
14	5.27	0.0246	0.0608	0.0635	0.0438	3.65	5400	6.75
15	5.24	0.0190	0.0800	0.0853	0.0570	6.20	9000	6.89
16	5.54	0.0246	0.0619	0.0630	0.0437	3.78	5400	7.00
17	9.14	0.0243	0.0410	0.0420	0.0288	6.70	3600	18.61
18	8.38	0.0252	0.0644	0.0641	0.0445	3.36	5400	6.22
19	8.05	0.0249	0.1106	0.1025	0.0738	2.18	9000	2.42
20	10.50	0.0450	0.0742	0.0761	0.0513	8.50	3600	23.61
21	8.65	0.0250	0.0863	0.0861	0.0593	4.87	7200	6.76
22	9.47	0.0300	0.1332	0.1340	0.0922	4.60	9000	5.11
23	5.22	0.0134	0.0694	0.0735	0.0476	7.15	10800	6.62
24	8.24	0.0247	0.0888	0.0865	0.0606	3.25	7440	4.36
25	9.34	0.0246	0.0644	0.0644	0.0437	9.57	5400	17.72
26	10.00	0.0225	0.1940	0.1900	0.1320	4.43	18000	2.46
27	5.48	0.0250	0.0656	0.0651	0.0442	3.63	5400	6.72
28	10.00	0.0430	0.4370	0.3980	0.2934	5.20	22600	2.41
29	16.15	0.0452	0.0810	0.0775	0.0536	2.80	3900	7.18
30	9.20	0.0229	0.0411	0.0400	0.0272	6.86	3600	19.05
31	9.21	0.0250	0.0742	0.0752	0.0491	4.10	6000	6.84
32	7.97	0.0248	0.0669	0.0620	0.0440	1.87	5400	3.46
33	6.05	0.0253	0.0683	0.0672	0.0450	3.48	5400	6.45
34	11.93	0.0240	0.0727	0.0710	0.0477	10.53	6000	17.55
35	8.20	0.0243	0.1530	0.1420	0.1006	4.30	12600	3.41
36	9.15	0.0251	0.0950	0.0973	0.0620	5.15	7500	6.87
37	9.26	0.0136	0.0310	0.0321	0.0202	7.84	4500	17.50
38	8.96	0.0350	0.1964	0.1830	0.1288	4.71	11700	4.02
39	9.00	0.0253	0.0924	0.0924	0.0601	5.80	7200	8.05
40	9.45	0.0400	0.1942	0.1800	0.1260	5.45	9000	6.06
41	7.90	0.0241	0.0880	0.0805	0.0575	2.30	7200	3.19
42	8.80	0.0194	0.0710	0.0703	0.0460	5.14	7200	7.14
43	8.96	0.0290	0.1840	0.1740	0.1200	5.45	12600	4.33
44	9.85	0.0420	0.1860	0.1740	0.1210	7.90	9000	8.79
45	10.00	0.0450	0.0782	0.0740	0.0505	3.60	3600	10.00
46	11.80	0.0236	0.0879	0.0828	0.0560	6.29	7260	8.66
47	9.37	0.0301	0.0837	0.0804	0.0535	3.89	5400	7.19
48	9.26	0.0133	0.0434	0.0430	0.0275	10.30	6300	16.35
49	8.45	0.0247	0.0924	0.0863	0.0585	2.95	7200	4.10
50	6.04	0.0252	0.0483	0.0440	0.0299	2.40	3600	6.66
51	8.95	0.0144	0.0548	0.0555	0.0341	5.30	7200	7.36
52	8.99	0.0194	0.0746	0.0720	0.0464	4.50	7200	6.25
53	12.00	0.0234	0.0904	0.0802	0.0558	3.05	7200	4.24
54	9.75	0.0200	0.0789	0.0749	0.0474	4.95	7200	6.12
55	9.31	0.0247	0.0967	0.0921	0.0585	4.80	7230	6.64
56	11.98	0.0140	0.0498	0.0477	0.0291	10.97	6300	17.42
57	8.46	0.0180	0.1397	0.1266	0.0824	7.60	14400	5.28
58	11.77	0.0137	0.0706	0.0636	0.0405	7.85	9000	8.73

TABLE X—(*Continued*)

No.	A	Percent Cuprous	$10^3 \times$ [Cupric]	$10^3 \times$ {Cupric}	$10^3 \times$ {Cuprous}	$10^3 \times$ {Cuprous}	$10^3 \times$ {$\bar{Cl}$}	$\bar{\gamma}$	$10^{-4} \times K$
1	15.0	25.5	0.235	3.84	0.161	0.95	11.08	0.294	3.1
2	18.0	28.0	0.383	4.26	0.300	1.34	7.35	0.326	1.9
3	18.0	29.2	0.214	3.40	0.176	1.23	12.47	0.283	2.6
4	18.0	30.3	0.382	3.42	0.322	1.42	7.24	0.328	1.5
5	18.0	31.5	0.073	2.42	0.077	1.13	8.14	0.320	1.8
6	23.5	34.2	0.060	1.22	0.064	0.58	8.20	0.319	3.4
7	47.0	35.2	0.119	0.71	0.130	0.40	5.07	0.485	1.9
8	47.0	35.4	0.119	0.71	0.132	0.40	5.31	0.376	3.0
9	18.0	36.5	0.315	3.11	0.355	1.66	11.05	0.295	1.3
10	18.0	37.2	0.047	1.56	0.052	0.92	5.97	0.348	2.4
11	47.0	37.7	0.212	0.78	0.252	0.74	4.54	0.615	0.8
12	47.0	37.7	0.120	0.69	0.146	0.43	5.05	0.490	1.5
13	47.0	38.7	0.113	0.66	0.146	0.44	5.01	0.500	1.4
14	47.0	39.0	0.115	0.66	0.146	0.44	5.02	0.500	1.4
15	47.0	40.6	0.086	0.40	0.117	0.35	5.10	0.475	1.4
16	47.0	42.0	0.106	0.63	0.152	0.46	5.21	0.400	1.8
17	18.0	42.0	0.039	1.39	0.057	0.89	8.28	0.319	1.7
18	23.5	43.2	0.117	1.16	0.186	0.87	7.65	0.323	1.5
19	23.5	43.6	0.267	1.18	0.531	1.28	7.21	0.328	0.7
20	35.2	45.0	0.053	1.23	0.085	0.35	9.63	0.308	1.8
21	23.5	45.5	0.104	1.10	0.174	0.87	7.90	0.320	1.4
22	37.5	46.0	0.175	0.97	0.280	0.81	8.90	0.313	0.7
23	47.0	46.0	0.057	0.32	0.096	0.28	5.05	0.490	1.7
24	23.5	46.5	0.157	1.13	0.273	0.97	7.48	0.325	1.1
25	18.0	47.3	0.038	1.28	0.068	0.99	8.31	0.318	1.3
26	35.2	48.0	0.025	0.82	0.440	0.85	9.52	0.309	1.2
27	47.0	48.0	0.099	0.57	0.185	0.55	5.18	0.425	1.1
28	35.2	49.0	0.453	1.49	0.433	0.83	9.07	0.311	2.2
29	18.0	51.1	0.147	2.10	0.306	2.00	13.94	0.274	0.7
30	18.0	51.1	0.031	1.11	0.064	0.99	8.14	0.320	1.1
31	47.0	51.2	0.092	0.54	0.192	0.58	8.77	0.315	1.8
32	23.5	52.0	0.268	1.05	0.377	1.14	7.09	0.329	0.8
33	47.0	52.0	0.098	0.55	0.210	0.61	5.62	0.360	1.1
34	18.0	52.3	0.034	1.18	0.075	1.08	10.72	0.299	1.1
35	23.5	52.5	0.175	1.02	0.384	1.15	7.33	0.327	0.8
36	47.0	53.0	0.089	0.52	0.201	0.61	8.68	0.315	1.4
37	18.0	53.5	0.019	0.63	0.043	0.62	8.57	0.315	1.6
38	37.5	53.6	0.204	0.94	0.451	1.12	8.12	0.319	0.7
39	47.0	53.8	0.075	0.51	0.175	0.59	8.53	0.316	1.5
40	35.2	54.0	0.167	1.12	0.393	1.31	8.36	0.318	0.7
41	23.5	54.0	0.184	1.02	0.417	1.20	7.01	0.330	0.7
42	47.0	54.4	0.064	0.39	0.153	0.47	8.43	0.317	1.7
43	37.5	54.5	0.162	0.78	0.370	0.95	8.30	0.317	0.9
44	30.5	55.0	0.111	1.13	0.259	1.29	8.64	0.314	0.7
45	35.2	55.4	0.099	1.03	0.242	1.17	8.88	0.313	0.8
46	18.0	55.9	0.062	1.06	0.157	1.20	10.52	0.300	0.8
47	47.0	56.4	0.094	0.57	0.244	0.76	8.76	0.315	1.0
48	18.0	57.8	0.014	0.44	0.049	0.66	8.54	0.316	1.0
49	47.0	58.0	0.131	0.51	0.360	0.79	7.94	0.320	0.8
50	47.0	61.3	0.075	0.43	0.241	0.71	5.51	0.366	0.7
51	47.0	61.4	0.040	0.25	0.123	0.39	8.63	0.316	1.6
52	47.0	62.2	0.161	0.87	0.203	0.56	8.55	0.316	2.7
53	18.0	62.5	0.109	0.96	0.357	1.51	10.55	0.299	0.5
54	47.0	62.8	0.049	0.26	0.195	0.55	9.25	0.310	0.9
55	47.0	64.7	0.067	0.38	0.250	0.74	8.71	0.315	0.7
56	18.0	71.1	0.012	0.40	0.059	0.85	10.96	0.295	0.6
57	30.5	71.2	0.052	0.35	0.119	0.40	7.76	0.321	2.1
58	18.0	74.3	0.021	0.29	0.076	0.58	10.72	0.299	1.0

trolyte. In these experiments equation IX assumes the form:

$$\frac{\{\overset{++}{Cu}\}}{\{\overset{+}{Cu}\}^2} = \frac{\frac{(2Q-P)}{63.6}\left(\frac{1}{V} + \frac{10^3 l}{k_2 A t}\right) + 0.171 \times 10^{-3}}{\left[\frac{2Y(P-Q)}{63.6}\left(\frac{1}{V} + \frac{10^3 l}{k_1 A t}\right)\right]^2}. \quad (IX a)$$

In the Introduction the qualitative effect of changes in rate of stirring was discussed. Table XII gives the data for three electrolyses which were carried out with lower rates of stirring than that used in the other experiments. Under R is given the rate of stirring in revolutions per minute, and in the last

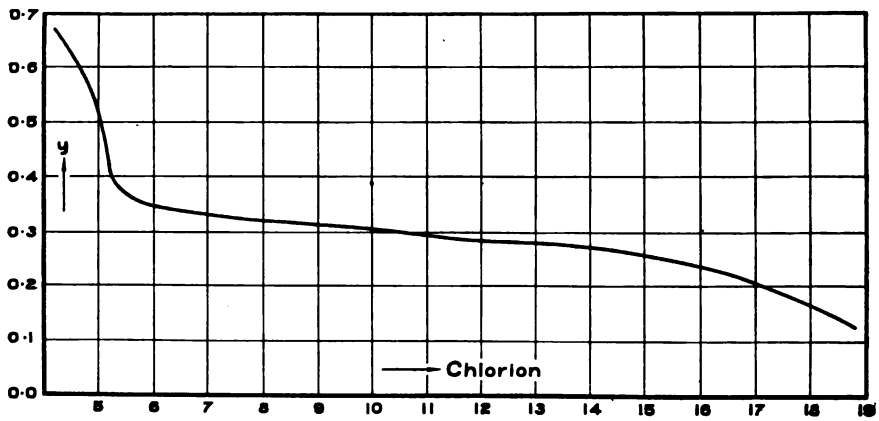

Fig. 2

column of the table, under C, is given the number of an experiment in Table X in which all the other variables were the same and which may thus be used for comparison. These experiments show that in accordance with the requirements of the theory the proportion of cuprous salt formed is less when the rate of stirring is decreased.

TABLE XI

Concentration of $\overset{++}{Cu}$ in stock solution, 0.171×10^{-3} mols per liter. Area of electrode = 23.5 cm². R = 1600. Room temp.

No.	$10^3 \times$ [Cl]	I (Amp.)	P obs.	Q	V	t	$10^4 \times V/t$	Per-cent Cu-prous
1	9.31	0.025	0.0990	0.0590	5.55	7200	7.64	67.7
2	9.31	0.025	0.0448	0.0290	5.23	3600	14.50	54.5
3	9.16	0.018	0.0728	0.0443	5.20	7200	7.23	64.3
4	9.20	0.018	0.0739	0.0450	5.65	7200	7.89	64.3

No.	$10^3 \times$ [Cupric]	$10^3 \times$ {Cupric}	$10^3 \times$ [Cuprous]	$10^3 \times$ {Cuprous}	$10^3 \times$ {$\overset{-}{Cl}$}	Y	$10^{-4} \times K$
1	0.396	2.83	0.229	1.253	8.05	0.320	0.6
2	0.382	4.73	0.095	0.288	8.34	0.318	1.2
3	0.219	0.71	0.172	1.138	8.27	0.319	0.6
4	0.216	0.71	0.169	0.904	8.30	0.319	0.9

TABLE XII

Area of electrode = 18 cms². Room temp.

R	$10^3 \times$ [Cl]	I (Amp.)	P	Q	V	t	$10^4 \times V/t$	Percent Cuprous	C
800	16.3	0.047	0.0896	0.0858	3.7	5400	6.86	4.3	29
1100	15.8	0.053	0.0681	0.0638	2.7	3600	7.50	7.0	29
1100	12.0	0.024	0.0804	0.0560	2.83	7200	3.92	43.5	53

In conclusion, I desire to express my thanks to Professor W. Lash Miller under whose direction the above investigation was carried out, for many valuable suggestions and kind encouragement during its progress.

SUMMARY

Having found that it was possible to make copper dissolve anodically in hydrochloric acid wholly as cupric or wholly as cuprous or as a mixture of these in any desired proportions depending upon the concentration of acid, current density, rate of stirring and rate of circulation of the electrolyte, it suggested itself that there may be equilibrium

at the surface of the anode between metallic copper and the cupric and cuprous salts in solution according to the equation,

$$\overset{++}{Cu} + \overset{0}{Cu} \rightleftarrows 2\overset{+}{Cu}.$$

A number of experiments were therefore undertaken to test this supposition quantitatively.

As the concentrations of the cupric and cuprous salts at the electrode were very different from those in the solution—sometimes they were twenty times as great—they had to be calculated from the latter by allowing for diffusion.

In these calculations there was required a knowledge of l/k_1 and l/k_2 (where l denotes the thickness of the diffusion-film and k_1 and k_2 are the diffusion constants of cuprous and cupric salts respectively). A method was therefore devised for obtaining these constants experimentally.

Electrolyses were carried out in which the concentration of hydrochloric acid was varied from 4.65×10^{-3} to 16.15×10^{-3} normal, the current from 0.013 to 0.051 ampere, the anode area from 18 to 47 cms^2, and the rate of circulation of the electrolyte through the cell varied from 0.242 to 2.361 cm^3 per second. It was found that the fraction of copper dissolved as cuprous varied from 25 to 74 per cent.

From the values of the concentrations at the electrode as calculated for all these experiments, values of the "constant" $K = \{\overset{++}{Cu}\}/\{\overset{+}{Cu}\}^2$ were determined. These were found to be in good agreement with the number deduced from the equilibrium experiments of Bodländer and Storbeck in which copper powder and cuprous chloride were shaken with solutions of potassium chloride.

Finally, the fraction of copper dissolved as cuprous salt at a rotating anode in hydrochloric acid, with varying conditions of concentration of acid, current density, rate of rotation and rate of circulation of the electrolyte, was calculated from this theory and found to be in good accord with the experimental results.

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UNIVERSITY OF TORONTO STUDIES

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No. 94: THE CHEMICAL PHILOSOPHY OF THE HIGH SCHOOL TEXT-BOOKS, BY W. LASH MILLER

(REPRINTED FROM SCIENCE, N.S., VOL. XXXIV.)

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THE CHEMICAL PHILOSOPHY OF THE HIGH-SCHOOL TEXT-BOOK

AT the present time the conception of continuity or unity or uniformity plays a great part in all departments of science; not only that continuity in time postulated by geologists and paleontologists, but the idea that all the divisions and classes established by science are but convenient though perhaps indispensable tools of the human mind, while nature, the object of our study, is one and indivisible.

To take examples from biology: modern systematists agree that the conceptions genus, species, variety, race, shade into one another, so that what in one group are regarded as generic distinctions, in another are hardly allowed to differentiate species; the very word biology recognizes the non-existence of a boundary between animal and vegetable; and a group of workers of the present day are busy removing even the distinction between inanimate and animate.

This view of nature, though now so widely accepted, is by no means contemporaneous with the birth of modern science; it came in only when the study of the most striking—because extreme—objects or relations had been followed by that of the less strongly characterized connecting links; and its acceptance has been hindered, in many cases, by the prevalence of certain extra-experimental or extra-observational "explanation made up to account for the earliest stu ied, exceptional, phenomena.

Thus modern geology was preceded a period of explanation by "catastrophes and modern biology by a period in whi the theory of separate creation of each the Linnean species was elevated almo to the rank of a religious dogma; in bo cases the main difficulties the new vi (of continuity, as I am calling it) had encounter, were due to the wrench it c to break with the old familiar extra-e perimental theories or explanations. Th again was to be expected; the theori were invented by men whose minds we deeply impressed by certain observatio or relations, their object was to "explai these relations and keep them before t mind, so that the theories can hardly blamed if in addition they kept out of t mind more recently discovered facts wh existence their originators never suspect

Our own science has passed through similar evolution. Modern chemistry gan with the study of the most striking all chemical phenomena, the phenomena combustion; and just when these we robbed of much of their mystery by t discovery that like other chemical re tions they obeyed the law of conservati of weight, a new interest was awakened the discovery of phases of invariable co position, the typical chemical compoun whose study laid the foundations of qua titative analysis, and led to the remark

[1] Address of the vice-chairman of the Division of Inorganic and Physical Chemistry, American Chemical Society, Indianapolis meeting, 1911.

so-called laws of chemical combination which Dalton's atomic theory was invented to explain.

The existence of such compounds is familiar enough to us, but a century ago one of the most celebrated chemists of his day strove for eleven years to show that no such things could be. This may serve as a measure of the interest and attention attracted by these substances at the time of their discovery; no wonder they alone were designated "chemical" compounds, small blame to those who thought that substances so striking in some respects must prove unique in all; how natural that the idea of continuity advocated by the defeated Berthollet should be forgotten, most natural that the extra-experimental theories invented at the beginning of the nineteenth century should make a sharp distinction between these chemical compounds and all else.

They did so; and as all good theories of that type do, they kept men's minds on the facts they were invented to explain; while the slowly accumulating "exceptions"—facts out of harmony with the tendency of the theory—being unexplained, and thus lacking a powerful aid to publicity, failed of their due influence on opinion. The discovery of the dissociation of chemical compounds by Deville and Debray—that marble, for instance, could be formed or broken up by the action of an air-pump—had surprisingly little effect at the time; but the work of Horstmann, Gibbs and van't Hoff, not to mention lesser lights by name, has at last made it abundantly clear that the "affinity of the atoms" which binds together the constituents of chemical compounds is subject to the same laws and may be measured in the same way as the forces —hitherto deemed distinct—which are responsible for the formation of solutions and adsorpta.

Thus, hand in hand with the study of *chemical equilibrium, the* idea of continuity entered chemistry, and has transformed it.

The high-school text books, however, as a class, in their tendency deny this continuity *in toto.*

In them the chemical compound and the element ("chemical individuals" for short) retain their former place as "the only two distinct kinds of matter"; and mechanical mixtures are distinguished by being separable into their ingredients "by mechanical means," thus ignoring the fact that mechanical means have been found for separating the ingredients of whole groups of chemical compounds, and the modern view that the amount of mechanical work necessary to bring about the separation is the only measure we have of the affinities that brought about their union.

Solutions, in some of these books, are openly classed with the mechanical mixtures, and in all are spoken of in language applicable properly to the latter alone. In brine, for instance, salt and water are said to "retain their properties unchanged." Not to dwell on the ridiculous illustration found in many, that "the salt retains its taste"—as though dry salt could be tasted—this assertion ignores the lowering of the vapor tension of the water, and consequently the lowering of its most characteristically "chemical" property, its chemical potential, or power to enter into reaction. Pure water, to give an instance, reacts at 30° C. with the chemical compound sodium sulphate to form its hydrate Glauber salt, also a chemical compound; the reaction is thus "chemical" in the strictest sense of the word, as none but chemical compounds are involved; when combined with salt to form a saturated brine, however, this power of the water is lost.

The change of chemical properties which is ignored when a solution is formed, is exaggerated when a chemical compound is the result of the union; in that case, "an entirely new substance" is produced, whose

constituents have "lost their characteristic properties." Now, surely, the most characteristic property of oxygen is to oxidize; does it lose the power of oxidizing carbon by combining with copper? if so, how are the "combustions" of the organic laboratory to be accounted for? Does it lose this power by combining with hydrogen? if so, what about the manufacture of water gas? In truth, as was the case with water in brine, the characteristic properties of oxygen in copper oxide and in water are lessened, not lost. It is not even safe to say that chemical combination always brings about the greater change; as Bell has shown, water combined in washing crystals is more "itself" than when sucked up by a dry cigar.

It might be urged in extenuation of this exaggeration, that, after all, chemistry, like other sciences, works by classification, and that children like distinctions sharp. The heroes of boys' books are heroes every inch; their fools and villains likewise Simon pure; and all agree that problem plays—where the problem is to tell the villain from the fool and to guess who is the hero—are not for such as they; a little exaggeration might therefore be defended as good pedagogy, and suited to the childish mind. This might be a good excuse, if it were not that (no doubt in order to be up to date) the texts while denying continuity, include much of the experimental evidence which has forced this conception into our science. The result is that they contradict themselves, and involve the whole subject in a maze of vagueness and mystification foreign to the scientific spirit; an example or two of each will be given, beginning with a typical instance of self-contradiction.

Most of the texts give their readers the impression that gunpowder is regarded as a mixture containing niter, or that sulphur and iron filings form a mixture containing sulphur, or that the high-sch grocers' mixture of sand and sugar is mixture containing sugar *because* t niter or the sulphur or the sugar can leached out or dissolved by water or carbon bisulphide, that is, by liquids whi dissolve those solids when pure. It sometimes added that the ingredients the mechanical mixture have thus be separated by the "mechanical operatio solution. And yet, every high sch chemistry gives instances of solid chemi compounds decomposed by water, a some even speak of the hydrolysis of sa like bismuth nitrate, which can be form by bringing together bismuth hydrate a nitric acid of the proper concentration a from which by treatment with water the nitric acid can be removed, leaving bismuth hydrate behind. Such instan of self-contradiction (where the ma premise of some argument is quietly ne tived elsewhere in the book) are scatte broadcast. "In spite of the most caref ness," to quote from the advertisement a new German balance, "the rider fall"; and the most carefulness has c tainly been employed in books which syrup instead of brine in their illust tions out of respect for the ions, and wh the Roozeboom diagram has driven to s stitute platinum for iron in the old m leading statement that "powdered ir magnetized iron, glowing iron and melt iron are just as truly iron" as a c poker. For one illustration is as bad another if it is used to confound solutic with mechanical mixtures, or to obsc the fact that chemical properties char with the temperature, and in some ca are measurably affected even by fine gri ing.

The vagueness of the texts, already ferred to, serves to keep their self-cont diction in a measure hidden. If ev statement is indefinite, all can be res

ciled; and what could be less definite than the customary definition of an element as a substance from which "nothing simpler than itself" can be obtained, if the meaning of "simpler" is left to be guessed? Unless perhaps it be the definition of a molecule as "the smallest quantity of a compound that can exist alone," or the corresponding indefinitions of atom, affinity, stability, valence, solvent and solute.

This vagueness is, naturally, most marked just where clearness of thought and precision of statement would show the untenability of the exceptional position assigned to the chemical individual; so that it is hardly surprising to find that not one of the texts gives a working definition (*i. e.,* one that can be applied in the laboratory) of the very group of substances which figures so prominently in all of them.

One of the Best Sellers defines chemical changes as "those which involve a change in the composition of the matter," while "sugar may be dissolved in water, but neither the sugar nor the water is changed in composition." This book, like the rest of them, brings in all the usual extra-observational hypotheses to "explain" the ordinary "laws of chemical combination," but gives no explanation whatever of this most extraordinary use of the word "composition"; although on this indefinition of chemical change is based the definition of chemical compound, that of mechanical mixture, and by implication that of chemical affinity as well.

Let us enquire what significance is attached in the practise of the present time to the terms mechanical mixture and chemical compound; we shall then be in a position to appreciate the difficulty in which the text-books find themselves and from which they seek to escape by the employment of systematic mystification as an aid to teaching.

Mechanical mixtures which for years have posed in the pages of Dammer as chemical compounds, are by the application of the phase rule daily being removed. What criterion has been adopted in each of these cases? Stripped of technical terminology it is: Whenever the reacting power, or potential, of a given substance (say niter) at fixed temperature and pressure is not affected by bringing it together with certain other substances (sulphur, charcoal) the resultant body is to be classed as a mechanical mixture with the substance in question (niter) as one of the constituents. In the simple case of gunpowder it is sufficient to find whether or no the solubility of the niter, in water, for instance, remains unchanged; but in the most complicated cases the principle remains the same. The condition of comparison at constant pressure (comparison at constant volume is impossible with solids and liquids) excludes air and such-like "mixtures of gases"; while whenever (as with arsenious sulphide and water) the change in chemical power is so slight as to remain in dispute, a discussion may arise as to whether the resultant "pseudo-solution" is to be classed with the solutions or with the mechanical mixtures—quite naturally, for at this point the two classes run into one another.

All this is simple and has proved important in practise; but being based on a view of solutions radically different from that of the texts under discussion, it can find no place in them.

The chemical compounds, or rather the substances so classed in the high school texts, may be grouped under three heads. First, silver chloride and other phases of invariable composition, which could be defined by adopting the "law" of combination in definite proportions as the definition of the group; second, water and similar bodies, which though not phases of in-

variable composition, can be "purified" by fractionation without paying special regard to the pressure at which the distillation is carried out; and third, a group of which sulphuric acid may be taken as the type. In the text books, the "chemical compound" sulphuric acid is described as "an oily liquid of s.g. 1.838 at 15° C."; it is in fact one of the continuous series of sulphuric acids—from dilute to fuming—used in the laboratory, and is thus not a phase of invariable composition; neither can it be "purified" by fractionation like water, while to include it among the chemical compounds because it freezes to a homogeneous solid of the same composition, would open the door wider than is consistent with general usage.

As a matter of fact, the name sulphuric acid and the formula H_2SO_4 were both introduced into chemistry without any special reference to the properties of this particular liquid, and would in all probability have won their way even if no substance of the composition H_2SO_4 could be prepared—such, at all events, was the case with the analogous "compounds" carbonic acid and ammonium hydrate. Formulas like H_2SO_4, H_2CO_3, NH_4OH and the names that go with them, are merely relics of one of the past attempts to represent symbolically the properties of solutions; in the old days, reagent bottles of sulphuric acid, whether concentrated or dilute, were labelled SO_3, then H_2SO_4 was substituted, and now, perhaps, $2\dot{H} + \bar{S}\bar{O}_4$, the symbol H_2SO_4 being retained with a different meaning. The change from one of these systems of formulation to another was due to a study of the properties of solutions as a class; can the text-books on their principles make this clear? Let us see how they deal with symbols.

The symbols HCl, $AgNO_3$, HNO_3 and AgCl are defined to give the compositions and, when known, the vapor densities the compounds they represent. Follo ing these definitions the symbol

$$HCl + AgNO_3 = HNO_3 + AgCl$$

purports to record what happens wh hydrogen chloride, the gas, and silver n trate, the solid, are brought togethe Perhaps the change represented woul actually take place, if the conditions we favorable; let us assume that it woul Throughout the books, however, equatio of this type are employed to represent r actions "in solution"; *i. e.*, in the case s lected, when hydrochloric acid (a solutic of the gas in water) is poured into a aqueous solution of silver nitrate.

Now, it is obvious that the use of sym bols is just as legitimate in chemistry it is in mathematics; and although an e perienced analyst would attend to man matters not referred to in the symbo would use rather more hydrochloric aci and would expect to get rather less silv chloride than the quantities represente in the equation, yet considering its brevit the symbol gives a fairly accurate idea the quantities involved, it is therefore considerable practical use, and deserv careful explanation in the texts. No suc explanation is offered, and indeed none needed by those who regard solutions mechanical mixtures; in their eyes th water has as little right to representatic in the chemical equation as has the gla of the beaker in which the precipitation made.

From such a starting point, however, clear idea of the meaning of our prese formulation of solutions is not to b reached; the high school treatment of an monium hydrate and carbonic acid—di cussions of the probability of "chemic combination" between ammonia and wate for instance, without first fixing th meaning of the term—only makes thing

worse; and in the end we find the children "believing" in ions, or "disbelieving" in hydrates-in-solution, just as a few years before they believed in fairies. The idea that our present method of formulating solutions is but a more or less imperfect symbolic representation of laboratory facts, will come upon them later, if it ever comes upon them, like the discovery that Santa Claus is but a kind thought; one experience of that kind ought to be enough.

Bacon says—I quote at second hand through Huxley—that "truth comes out of error much more readily than out of confusion," and Freeman, speaking of history, says that "the difference between good and bad teaching mainly consists in this, whether the words used are really clothed with a meaning or not." Is chemistry so different? Are vagueness and dodging really necessary in the text-books of our science? They are, so long as in the theoretical part the conception of continuity is negatived, while in the practical part experiments are described which have forced that conception into the science.

A change is unavoidable; but it is wholly unnecessary to give up the interesting chemical experiments for prosy disquisitions on water, ice and steam, or to fill the book with "How Old Is Ann" thermodynamical problems adapted from van Laar. Striking phenomena are as interesting to beginners to-day as they were a hundred years ago, but gradations too exist, and their existence must not be denied.

Until this change is made, children will be trained to accept obscure equivocal and dogmatic statements in place of clear and exact thought, and to be glib with words they do not understand. Such discipline, enforced in the name of science, of our science, far from ensuring the results prophesied by those whose efforts obtained for these new studies the place they now occupy in the schools, can hardly fail to injure pupil and teacher alike, depriving them of mental self-reliance and the power to weigh evidence and think clearly.

Unless a change be made, chemistry will surely earn a place among that group of pedagogic processes which Huxley strove so hard to have displaced, and which he characterized as the direct and preventible cause of most of the world's stupidity.

W. Lash Miller

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PAPERS FROM THE CHEMICAL LABORATORIES

No. 95: LANTERN EXPERIMENTS ON REACTIONS IN NON-HOMOGENEOUS SYSTEMS, BY FRANK B. KENRICK

(REPRINTED FROM THE JOURNAL OF PHYSICAL CHEMISTRY, VOL. XVI)

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LANTERN EXPERIMENTS ON REACTIONS IN NON-HOMOGENEOUS SYSTEMS[1]

BY FRANK B. KENRICK

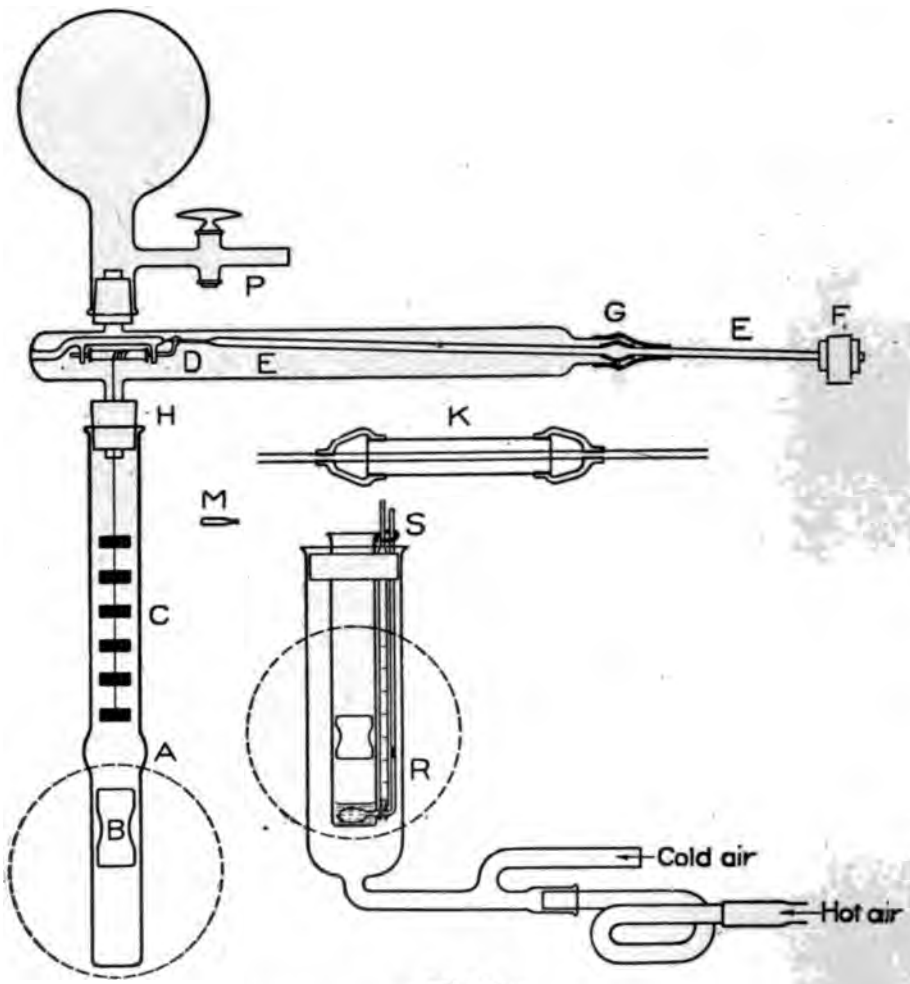
The use of graphs for expressing experimental relations has done much to simplify the teaching of general chemistry. A good diagram not only gives a concrete picture of a relation abstracted from tables of numbers but possesses also a peculiar fascination of its own for the average mind. A research student experiences a feeling of elation over his first experimental graph that is rivalled only by the sense of proprietorship of the organic chemist towards his first "new body." But in this very fascination there is a pedagogical danger. As the student's enthusiasm for the diagrams increases his interest in the troublesome chemicals often wanes; he begins to talk of melts moving along curves as if they were baseballs and to think of common salt existing in "fields" instead of in the sea.

To offset these dangers it has become the custom to draw diagrams of pistons and cylinders alongside the graphs, in the hope of keeping the balance between experiment and representation. With the idea of making these conventional cylinders and pistons more realistic the writer has used actual tubes containing the chemicals which may be thrown on the screen as working models.

The main difficulty in these experiments is in making an air-tight frictionless joint between the piston and cylinder. The only packing that the writer has found practicable is mercury, and since the leakage is prevented only by surface tension the pressures must be limited to comparatively small values. The four following experiments illustrate the use that may be made of these models.

[1] These experiments were shown for the first time at the Washington meeting of the American Chemical Society, December, 1911, in a lecture by Mr. H. E. Howe and the writer. The excellent Bausch & Lomb Convertible Baloptiicon was used in all the experiments; the arrangement of apparatus described in Nos. 5 and 6 applies particularly to this lantern.

1. Boyle's Law.—*A* is the cylinder tube (Fig. 1) in which the piston *B* fits loosely but closely. Both *A* and *B* are



-Fig.1- -Fig.2-

$\frac{5}{16}$ of full size

flattened at the bottom for appearance sake. *C* is a of lead weights (10 grams each), hung on a piece of thread, the upper end of which is wound round

winch *D*. The point of the rod *E* fits loosely into the little ring on the handle of the winch, which may be turned by moving the weight *F* in a small circle, there being a sufficient play at *G* to allow a slight side motion.

The apparatus is all put together with the exception of the joint *H*. The tube and piston are thoroughly cleaned and dried and about 7 mm of mercury is poured into *A*. A little bulb, *M*, open at one end and containing air, is dropped in and then the piston is inserted and pushed right down until enough mercury has been squeezed up to fill the waist. After connecting at *H* the apparatus is exhausted through *P* by an air-pump (a filter-pump is hardly sufficient). The air contained in the little bulb gradually expands and lifts the piston to the weights. If one weight is not sufficient to balance the pressure when the piston is at the edge of the field of the lantern, shown by the dotted line, the weights are cautiously raised till the piston reaches the expansion in the cylinder, when a few bubbles of air may be allowed to escape past the seal.

When the weights are lowered the piston should go down smoothly, a definite, but decreasing, distance for each additional weight. If it sticks it means that either the tube or mercury is dirty. A well selected piston of the dimensions shown will support a weight of 200 grams, without the seal giving way.

A few points may be noted in regard to making the apparatus. A length of tube is selected first for the cylinder by running a pair of calipers over the stock of glass. The exact size is less important than uniformity of bore. In choosing the piece for the piston it will generally be found that if the end of a stick of glass fits approximately, there will be one piece in the stick of the right size. A number of pieces about three inches long should be corked at one end and dropped into the closed cylinder. One that falls slowly as the air escapes and shows no tendency to stick, even when turned through various angles, should be chosen. In making the waist in the piston a rod should be sealed through the

tube as shown in Fig, 1, *K* and the whole rotated in a small hot flame. In this way the two ends are kept exactly concentric.

The lead weights should be painted with melted sealing-wax, otherwise they are sure to become amalgamated by the mercury and the mobility of the seal is spoiled. They may be strung on a thread, in which knots are tied at intervals, and made fast by pressing the lead round the thread with a pointed tool. A little hook on the barrel of the winch catches a loop in the end of the thread, which can be poked up through the tube at *H*. The weight *F*—a cork with a strip of lead round it—prevents the winch from unwinding. The rubber joints may be made tight with tap-grease.

When once set up the apparatus may be kept for a week or more ready for use, but requires occasional re-exhausting.

2. *Vapor Pressure.*—The apparatus is similar to that used in Exp. 1. The little bulb, *M*, is filled completely with freshly boiled water (which has just the right vapor pressure for the apparatus) and mercury is squeezed into the seal as in Exp. 1. In exhausting the apparatus water vapor should be allowed to bubble through the seal at the expansion until about half the water has evaporated out of the bulb, so as to get rid of the small quantity of air always left in the corners. If the water is not freshly boiled it is apt to flow out of the bulb on exhausting, and the bubbling past the seal becomes too violent and uncontrollable.

The piston should go smoothly up and down on lifting or adding one extra weight. By gently warming the tube by the hand or by a small flame more weights are lifted.

When freshly filled this apparatus works admirably, but after a day or so the piston is apt to stick slightly at the position in which it has been left. The writer has found it better to rub out the cylinder with a *slightly* oily cloth. The water vapor then always condenses on the mercury and not on the sides of the glass, and if the piston is left down when not in use the sticking is avoided.

3. *Vapor Pressure and Temperature.*—Several very in-

structive experiments may be made at atmospheric pressure with a simpler form of apparatus. See Fig. 2. The cylinder and piston may be made from two carefully selected test tubes, though closeness of fit is not so necessary as in the previous experiments. A bulb about the size of a pea on the end of a thin-walled capillary tube sealed through the cylinder near the bottom serves as an air-thermometer, the temperature being registered by the height of a drop of mercury, *R*. The upper end of the thermometer is protected from breakage by the hook of glass *S*, which also serves to hold the scale, made by drawing out a microscope slide and marking the figures with india ink.

Enough alcohol, or other liquid, to cover the thermometer bulb is poured into the cylinder without wetting the sides. By holding the piston about half way out of the top of the cylinder mercury may be poured into the seal. If the tube is then slightly inclined the piston may be pushed slowly down to the alcohol while the air bubbles up through the mercury. A small bubble of air should be left to prevent superheating. The top of the piston must be slightly turned in, to prevent the mercury bubbling over into the hollow of the piston.

The cylinder is hung loosely in a larger thin-walled tube, 4 cm in diameter, as shown in the diagram. The temperature can be slowly raised or lowered by a current of air, the heat being conveniently supplied by a heated copper tube, as shown, attached to the glass by asbestos paper. On raising the temperature to a certain point the piston rises; on cooling a few degrees it drops back. The thermometer scale need be graduated only very roughly as long as the 78 mark corresponds to the temperature at which the piston goes up. The superheating of a liquid may be shown, if, during the heating, the piston be pushed down several times so that the alcohol vapor bubbling through the seal carries out the remaining air. After now completely condensing the vapor the liquid may be heated well over the boiling point, until the piston is suddenly driven violently up to the top of the cylinder.

4. *Decomposition Temperature.*—The decomposition of powdered calcium chloride ammonia may be shown in the same apparatus as used in 3, but to get a reasonably sharp temperature the air must be expelled from the powder by pushing the piston down several times during the heating. This, however, must be done at the time of showing the experiment; for if the tube is once allowed to cool after the air is expelled the mercury will be sucked down from the seal into the powder.

It may be mentioned that in the last two experiments the thermometer must be inside the cylinder, because otherwise, unless the heating is very gradual—and this takes too long for a lecture experiment—the thermometer would become heated much more rapidly than the liquid. The use of a water bath to supply the heat is excluded by the refraction of the water. The apparatus is, no doubt, capable of further application, but it may be noted that subliming solids condense on the glass and cause sticking.

5. *Delayed Reactions.*—In connection with the superheating of the alcohol in Exp. 3, the analogy between the crystallization of a supersaturated solution on nuclei and the reduction of silver salts in photographic development may be shown as follows. The experiments have nothing to do with pistons and cylinders but may properly be described under the title of this article.

After placing a crystallizing dish in the vertical attachment of the lantern the bottom of the dish is written on with a crystal of copper sulphate. Although nothing is visible on the screen the writing may be "developed" by pouring into the dish a supersaturated solution of copper sulphate, made by cooling a solution saturated with this salt at 45° C to the ordinary temperature.

The experiment may be varied to show the meaninglessness of the use of the term "saturated solution" without specifying the substance in respect to which it is saturated. "Copper chloride" for example may be written on the dish with an alcoholic solution of copper chloride and allowed to dry, while "copper sulphate" is scratched over it with a

crystal of copper sulphate. On developing with the copper sulphate solution the words "copper chloride" are replaced by "copper sulphate."

It may not be generally realized that a solid projection lantern serves as an excellent lecture-room camera. In fact, the whole process of exposure, development and projection of the negative may be carried out in the lantern in less than three minutes. The lantern is focussed for the solid projection of a crystallizing dish, an orange screen[1] and an opaque card being placed between the projection cabinet and the lamp. A second lantern is arranged to give a "spot-light" on the screen in the exact position of the image of the crystallizing dish. A disc of developing paper (special velox) is placed in the dish and held down by a ring of glass. The subject to be photographed stands, or is placed, against the screen in the spot-light. After a sufficient exposure—about two minutes if the lantern is not too far from the screen—the spot-light is turned off and the opaque card drawn out of the other lantern, showing the dish and plain paper on the screen. A few seconds later the developer should be squirted into the dish through the peep-hole in the lantern box, and then the hypo solution, as soon as the image appears on the screen.

6. Arrangement of Lantern.—In the projection of glass apparatus the best results are obtained by placing the object in parallel light close *behind* the condensing lens *A*, Fig. 3. A convenient arrangement for the lantern for general purposes is shown in the same diagram. The two large mirrors on the stand *B* in front of the lantern rectify the image and throw it on a screen on the right hand wall of the lecture room. By reversing the positions of the mirrors *C* and *D*

[1] I am indebted to Professor A. H. Abbott, University of Toronto, for the following receipt for an excellent light screen. Three photographic plates are washed in hypo and dyed respectively with quinoline yellow, Indian yellow and methyl violet. The first two should be dyed as dark as possible, but the third should be only a faint violet shade. The three plates are used together.

in the vertical and solid projection attachments[1] the images from these are also thrown to the right. The "Schlieren" apparatus (see footnote, Exp.3,*b*, preceding article) may be used, at the same time arranging the lenses to the left of the lantern. By simply sliding the large mirrors *B* out of the way the image

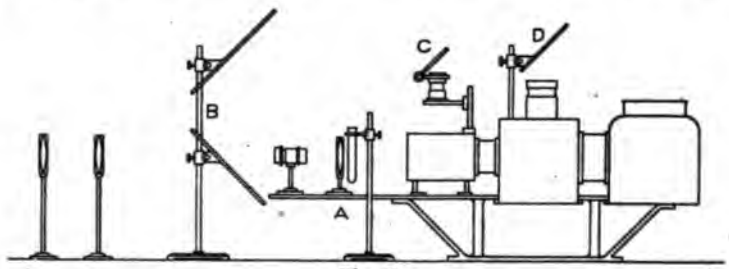


Fig. 3

is thrown on the left wall of the lecture room. The lantern may be placed well to the right of the lecture table, thus giving the necessary distance between screen and lantern required by the "Schlieren" apparatus.

University of Toronto, Chemical Laboratory,
March, 1912

[1] Messrs. Bausch & Lomb will supply their Convertible Balopticon with the slight modifications required for reversing the position of the mirror *D* and detaching the lens *A* from the vertical attachments.

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No. 96: SOME LECTURE EXPERIMENTS ON SURFACE TENSION, BY FRANK B. KENRICK

(REPRINTED FROM THE JOURNAL OF PHYSICAL CHEMISTRY, VOL. XVI)

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SOME LECTURE EXPERIMENTS ON SURFACE TENSION[1]

BY FRANK B. KENRICK

Surface tension affords abundant scope for attractive lecture experiments. The experiments outlined in this paper have been used for many years by the writer, and although less spectacular than many described in the literature, have been found very effective in making clear the principles of surface tension in its application to the chemical phenomena of solubility and adsorption.

1. *Mechanical Model.*—This serves to illustrate the definition of surface tension in work units as the maximum quantity of work that can be gained when a surface is decreased in area by one square centimeter. A projection cell 40 mm × 10 mm and 60 mm high, the upper edges of which have been coated with a film of paraffin wax, is filled almost to overflowing with water. On the surface is floated a thin shaving of cork 30 mm × 5 mm × 1 mm, to which is attached a fine cotton thread about 40 mm long terminating in a little glass hook. The thread passes over a small pulley made from a pill box and a pin resting in a double Y-shaped glass bearing. Three weights of glass or bent wire, weighing about 0.1 gram, 0.07 gram and 0.04 gram may be hung on the hook. The middle weight approximately balances the surface tension, while the lighter one on being pulled down with a pair of tweezers is lifted again by the surface tension. A fall of 1 cc produces one square centimeter of surface: *viz.*, 0.5 cm^2 on the forward under side of the cork which is wet with water and 0.5 cm^2 on the upper surface of the liquid in the cell. The whole of an apparatus of the size described may be pro-

[1] Expts. Nos. 1, 2, 4, 6 and 7 were shown at a local meeting of the American Chem. Soc. at Niagara Falls, January, 1909. 3(*a*) and 5 at a lecture at the Research Laboratory, General Electric Co., January, 1911, and 3(*b*) in a lecture by Mr. Howe and the writer at the Washington meeting of the American Chem. Soc., December, 1911.

jected with an ordinary lantern. While quantitative results cannot, of course, be expected, this is a useful experiment to have thrown on the screen when the meaning of surface tension is being explained. The fact is often overlooked that the definition of surface tension as the force acting across a line 1 cc long, etc., presupposes that there is a movable edge of surface to which a weight or other dynamometer can be attached, and that consequently the idea of surface tension at the boundary of a solid is excluded by this definition whereas the definition in terms of work is applicable to every case in which the area of surface can be changed by any reversible process for which the work can be determined.

2. *Two Drops.*—This is analogous to the well known experiment with large and small soap bubbles on the ends of a U-tube.[1] It is the writer's experience that soap bubbles work very well in the preparation room but generally burst at the critical moment in the lecture. Drops of water have not this disadvantage, and are more closely analogous to the chemicals whose behavior this experiment is designed to illustrate. (See 3.) The diagram (Fig. 1 A) shows suffi-

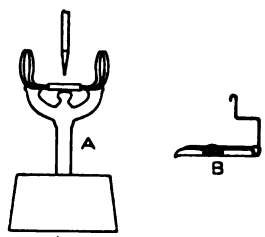

Fig. 1

ciently clearly the arrangement of the apparatus. The upper ends of the capillary tubes should be ground to flat discs about 1.7 mm in diameter and coated with paraffin wax. The two halves of the U-tube are connected by a piece of the fine rubber tubing (0.5 mm bore) used for covering spectacle frames. The U-tube is completely filled with water, and while the rubber connection is closed by pressure with a

[1] C. V. Boys: "Soap Bubbles," 1890, p. 55.

screw driver or other hard object, a small and large drop are piled up on the ends of the tube with a fine-pointed pipette. On releasing the pressure the large drop grows bigger at the expense of the small one. The whole apparatus may be projected with an ordinary lantern, or, if it is made very compact, with a low-power projecting microscope.

3. *Surface Tension and Solubility.*—This is a chemical application of the principle illustrated in Exp. 2. The increase in the solubility of gypsum caused by a fine state of division, first determined by Hulett,[1] may be shown as a lecture experiment in either of the two following ways:

(*a*) The following materials are required: a "*normally saturated gypsum solution,*" made according to Hulett's method, by stirring gently for some hours about 300 cc water with 30 grams coarsely powdered gypsum, from which the fine particles have been previously rinsed with water. This solution may be kept indefinitely, and shown in contact with the crystals. *Finely powdered gypsum,* made by grinding about a gram of the crystals to an *impalpable* powder in an agate mortar. *Sodium phosphate solution*; a solution is made up containing 100 grams sodium phosphate ($Na_2HPO_4.12H_2O$) and 2.5 grams sodium hydroxide per liter. About 29 cc of this solution (the exact amount must be found by trial) is colored dark pink with phenolphthalein and diluted with water to 100 cc.

The experiment is carried out as follows: To one of two beakers, each containing about 50 cc of normally saturated gypsum solution, is added a pinch (about 0.5 gram) of the finely powdered gypsum. This is shaken for a moment and then both[1] liquids are immediately filtered through previously arranged filters. The first filtrate may be poured through again if not perfectly clear. Twenty cc of each filtrate are then put in two projection cells in the lantern and shown on the screen. On adding 10 cc of the sodium

[1] Zeit. phys. Chem., 37, 385 (1901).

[2] It is best to treat both liquids in exactly the same way, since the point of the experiment is to show a small difference in concentration.

phosphate solution to each cell, the liquid which was shaken with the gypsum turns colorless while the other remains pink. The experiment takes only two minutes to perform; if more time is available for filtration, etc., it may be carried out on a larger scale without the lantern, and an actual titration made, by which a difference of 10 percent can be shown in the concentrations.

(*b*) The above experiment may be shown more strikingly by the use of an adaptation of Töpler's "Schlierenapparat" to lantern projection,[1] by which concentration streams in a liquid are made visible on the screen. A flat cell containing water, with a transparent gypsum crystal hung just below the surface, is first projected with the lantern. As the gypsum dissolves, a narrow stream of solution is seen flowing down from the lowest point of the crystal. Next the crystal is hung in the normally saturated gypsum solution; no stream is visible. Finally a little glass trough containing a pinch of the finely powdered gypsum is hung in a slightly inclined position in the same cell. In a few seconds a stream of concentrated solution is seen flowing down from the lower end of the trough. The trough may be made by splitting a small thin-walled glass tube and sealing a glass hanger to it as shown in Fig. 1, *B*.

The writer has tried to show, by this means, the simultaneous solution and crystallization of gypsum in a slightly "supersaturated" solution, but the rate of separation of the gypsum is so extremely slow compared with the rate of solution that streams of weaker solution could never be seen rising from the crystal.

4. *Surface Concentration in Saponin Solution.*—A very simple experiment showing that the surface tension of a freshly formed surface of saponin solution is practically the same as that of water may be carried out as follows. Two beakers are filled to exactly the same depth of about 2 one with water and the other with a saponin solution

[1] A description of this will shortly appear in THIS JOURNAL by Miller and the present writer.

taining 0.2 gram per 100 cc. A glass tube of 2.5 mm bore and 20 cm long, with the lower end cut off obliquely, is held upright in the water with the end resting on the bottom of the beaker, a piece of thread having been previously tied round the tube to mark the height to which the water rises. The effect of sucking up the water in the tube and letting it fall is first shown on the screen. The same thing is then done with the saponin solution. The liquid drops rapidly as before, pauses a moment at the high water mark and then falls slowly to a much lower level corresponding to the normal surface tension of the solution.

5. *Surface Concentration of Methyl Violet Solution.*—During the last few years several experiments have been described giving direct evidence of surface concentration in certain solutions, and quite recently Donnan and Barker[1] have made a quantitative investigation of this phenomenon. The surface concentration in methyl violet solution may be demonstrated by the following lecture experiment:

300 cc of an aqueous solution of methyl violet (0.25 gram per liter) are shaken vigorously in a 1 liter separating bulb so as to produce a foam, and then allowed to stand for four minutes to allow the liquid to drain away from between the bubbles. The clear liquid is next drawn off into a beaker and the foam allowed to subside until more than 1 cc of liquid has collected above the tap, which will require perhaps three or four minutes longer. The settlings are then drawn off into a second beaker. By diluting exactly 1 cc of each liquid with 20 cc of water, and placing the diluted liquids in a double glass cell (1 cm thick) before the lantern, the color of the foam settlings is seen to be slightly, but unmistakably, darker than the unfoamed liquid.

The time required for the foam to subside varies. If it should take too long the process may be hastened by gentle stirring, through the mouth of the separating bulb, with a glass rod moistened with amyl alcohol. This amount of amyl alcohol does not itself affect the color of the liquid.

[1] Proc. Roy. Soc., 85 A, 557 (1911).

6. *Emulsification of Oil by Potash.*—This may be shown rather strikingly as follows: A strip of fine copper or iron gauze is folded on itself four or five times so as to make a pad which fits into the bottom of a projection cell (1 cm thick). About 20 drops of olive or linseed oil are allowed to soak into the gauze pad from a pipette, care being taken to keep the sides of the cell free from oil. The cell is then filled about 4 cm deep with water. When this is projected on the screen the oil is seen protruding in little humps through the meshes of the gauze, but the water-oil surface tension prevents it floating up through the water. Directly a little potash solution is added to the water the humps of oil elongate and flow in a number of thin streams to the surface where they form an emulsion.

7. *Oil-films on Water.*—This experiment shows that the action between oil and water is purely a surface phenomenon. A glass rod, round which is stuck a label rubbed with linseed oil, is supported about 3 cm above the bottom of a 300 cc beaker. Tap water is allowed to run into the beaker and flow over the edges until the surface is clean enough to show camphor movements. If the beaker is placed in front of the condensing system of a lantern, with the surface of the liquid well above the centre of the field, the moving camphor can be plainly seen on the screen. If, now, bubbles of air are blown into the water from a clean tube they have no effect on the camphor movements so long as they do not touch the oil, although they stir the liquid, but as soon as they are allowed to brush up past the rod the movements cease.

University of Toronto, Chemical Laboratory,
March, 1912

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PAPERS FROM THE CHEMICAL LABORATORIES

No. 97: THE PHTHALYL CYANIDES, BY GIBBS BLACKSTOCK

(REPRINTED FROM THE JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, VOL. 34)

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THE PHTHALYL CYANIDES.

By Gibbs Blackstock.

Received June 4, 1912.

Some time ago Mr. C. H. Robinson, in this laboratory, prepared phthalyl cyanide in the hope of obtaining from it, by hydrolysis, the corresponding dibasic acid, but his work was interrupted before completion. The

[1] *Am. Chem. J.*, 26, 289 (1901).

author has repeated and extended Mr. Robinson's work and also prepared and studied isophthalyl cyanide and terephthalyl cyanide.

Three methods were used for the preparation of the cyanides.

I. The method used by Claisen[1] for the preparation of benzoyl cyanide. The acid chloride was dissolved in about three times its weight of anhydrous ether and to this was added about twice the calculate amount of anhydrous hydrogen cyanide and a slightly larger excess of pyridine was then added gradually to the ethereal solution. In each case a white precipitate was immediately thrown down, which gradually disappeared and at the end of one to two days the crude cyanides had completely separated out as dark viscous oils. This white precipitate appears to be a product of the acid chloride and pyridine and will be further investigated.

II. The acid chloride and mercuric cyanide in acetone solution were boiled for several hours with reflux condenser. This method did not give satisfactory yields and was abandoned.

III. The acid chloride was heated in a sealed tube with excess of mercuric cyanide for 5–7 hours at 140–160°. Mercuric cyanide gave much better results in this method than potassium cyanide.

The three isomeric cyanides are very similar in properties. They are all brown powders, soluble in acetone, alcohol, pyridine, ammonia and potassium hydroxide solution and insoluble in water, ether, benzene, ligroin and dilute acids. They become viscous at temperatures in the neighborhood of 300°, with apparent decomposition. When heated in a sealed tube with conc. hydrochloric acid they were not hydrolyzed, but with 15–20% potassium hydroxide solution either in sealed tubes or with reflux condenser they gave a slight odor of ammonia which probably indicated slight hydrolysis of the nitrile.

Phthalyl Cyanide.—16 grams pyridine were added, gradually to a solution of 10 grams phthalyl chloride and 5 grams hydrogen cyanide in 25 cc. ether. After 2 days the viscous mass was dissolved in ammonia, precipitated by acidification and washed with hot water. Yield, 3.6 grams (40%). The phthalyl cyanide prepared by this method was always found to be too high in nitrogen unless very carefully purified.

Ten grams phthalyl chloride and 16 grams mercuric cyanide were heated in a sealed tube for 6 hours at 140–160°. The product was dissolved in acetone and precipitated with ether, then dissolved in ammonia and purified as above. Yield, 4.4 grams (50%).

Isophthalyl Cyanide.—Ten grams isophthalyl chloride were dissolved in 30 cc. ether, 3 grams hydrogen cyanide added and then, gradually, 16 grams pyridine. The crude cyanide was dissolved in ammonia, pre-

[1] *Ber.*, 31, 1023.

cipitated by hydrochloric acid, washed with water, again dissolved in ammonia and reprecipitated by boiling off the ammonia. Yield, 3.5 grams (40%).

Five grams isophthalyl chloride was heated in a sealed tube with 8 grams of mercuric cyanide for 6 hours at 200°. Yield, 1.7 grams (30%)

Calculated for $C_6H_4(COCN)_2$: N, 15.2. Found: N, 15.0.

Terephthalyl Cyanide.—Ten grams terephthalyl chloride were dissolved in 25 cc. ether, 4 grams hydrogen cyanide added and 16 grams pyridine. The cyanide was purified in the same manner as the isophthalyl cyanide. Yield, 4 grams (45%).

In the sealed tube, 4 grams terephthalyl chloride and 7 grams mercuric cyanide gave 1.2 grams (30%).

Calculated for $C_6H_4(COCN)_2$: N, 15.2. Found: N, 15.2.

The first method of preparation is not recommended for phthalyl cyanide, as there is a product rich in nitrogen from which it is hard to purify it, but in the other cases it gives better yields than the preparation from mercuric cyanide.

These experiments were carried out under the direction of Professor F. B. Allan.

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(REPRINTED FROM THE TRANSACTIONS OF THE AMERICAN ELECTROCHEMICAL SOCIETY VOL. XXI)

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A paper presented at the Twenty-first General Meeting of the American Electrochemical Society, in Boston, Mass., April 20, 1912, President W. R. Whitney in the Chair.

THE INFLUENCE OF DIFFUSION ON ELECTROMOTIVE FORCE PRODUCED IN SOLUTIONS BY CENTRIFUGAL ACTION.

By W. Lash Miller.

In reading Tolman's account of his measurements of the electromotive force produced in solutions by centrifugal action,[1] I noticed that the equations for the electromotive force were deduced without allowing for any possible differences in concentration at the two ends of the tube produced by the whirling;[2] as in some of his experiments these differences would become very considerable if the rotation were sufficiently prolonged, it seemed possible that even in a few minutes the "concentration cell" effect might become measurable, and that it might perhaps account for the "residual electromotive force" observed by him.

The calculations carried out in the following paragraphs show, however, that the polarization produced by concentration changes in short periods of centrifuging is very slight. During the rotation both iodine and iodide keep increasing in concentration at the outer electrode and decreasing at the inner, but the E.M.F. that would be produced by an increase of one percent in the concentration of the iodine alone is almost counterbalanced by a rise of one-third percent in the concentration of the iodide; and, as will be shown, the iodine concentration rises, at first, just about three times as rapidly as that of the iodide; so that the E.M.F. actually generated is very small, much too small to account for the "residual" voltage observed by Tolman.

As, so far as I am aware, no attempts have hitherto been made to calculate the rate at which diffusion would take place under the influence of centrifugal force, a short account of the method which I have adopted may prove of interest. Briefly stated, it consists (*1*) in determining the distribution of concentrations along

[1] Proc. Am. Acad. Arts and Sci., **46**, 109 (1910). Jour. Am. Chem. Soc.

[2] Acad., *loc. cit.* p. 116, foot note.

the tube when equilibrium has been reached (*i. e.*, when the solution has been whirled for an "infinite" time) by the usual thermodynamic method; (*2*) in treating this equilibrium as due to the equality of two "virtual" rates of flow, one (towards the axis) due to concentration gradient, and the other (toward the periphery) due to centrifugal force; (*3*) in expressing the former of these by Fick's equation for the rate of diffusion along a fall of concentration, and thus (*4*) finding a plausible expression for the second or virtual flow due to centrifugal force. Assuming, then, that the actual flow at any moment is represented by the algebraical sum of the two components, expressions for which have thus been obtained, (*5*) a differential equation is set up, and a solution obtained to suit the conditions of Tolman's experiments.

The method just described is employed in calculating the rate of diffusion of the potassium iodide in solutions originally normal with regard to the iodide and fiftieth normal with regard to free iodine, the effect of the small quantity of iodine on the diffusion of the iodide being neglected. In calculating the rate of diffusion of the iodine in the same solutions, however, it had to be remembered that, in the absence of centrifugal force and of iodine-concentration difference, iodine will diffuse from a dilute to a concentrated solution of potassium iodide. This fact, which is taken account of in the present system of chemical formulas by distinguishing between "dissolved I_2" and "$\overline{I_3}$," is here allowed for by introducing a third "virtual flow," that due to iodide-concentration difference, as explained below.

POTASSIUM IODIDE, CONCENTRATIONS AT EQUILIBRIUM.

The distribution of concentration along the centrifugal tube when equilibrium is reached is given by the expression

$$\mu - \frac{2\,\pi^2 N^2\,(1-vd)\,x^2}{981 \times 42660} = const. \qquad (1)$$

where μ is Gibbs' thermodynamic potential; it may be replaced by

$$\frac{1.98\theta}{F}\ log.\ nat\ z + const.$$

[N is the number of revolutions of the axis per second; θ the thermodynamic temperature, 293 in Tolman's experiments; F the thermodynamic

formula weight, assuming 78 percent dissociation $F = 166/1.78$; z is the concentration of the iodide, as only ratios occur in the formulas, any units will do; v the "partial volume" (Tolman) of the iodide $= 0.284$; d, the density of the solution, $= 1.115$; $\pi = 3.1416$; the divisor 981×42660 converts ergs to calories; 1.98 is the gas constant.]

whence, neglecting the change of vd with the concentration,

$$[at\ equil.]\ z = Ae^{\beta x^2};\ where\ \beta = 5.180 \times 10^{-8} N^2 \quad (2)$$

Since the total amount of iodide in the tube remains constant,

$$\int_r^R z dx = z_0(R - r);\ whence\ A = z_0(R - r) / \int_r^R e^{\beta x^2}\, dx \quad (3)$$

[z_0 is the initial concentration of the iodide, uniform throughout the tube, (normal, in Tolman's work); r (Tolman's r_1) the distance of the inner electrode from the axis, and R (Tolman's r_2) that of the outer electrode, both in centimeters. As the outer electrode fitted the end of the tube and the inner electrode had almost the same cross section as the tube, r and R give the distance of the effective inner and outer ends of the column of solution from the axis. In the experiments with potassium iodide and iodine, $r = 4.3$ and $R = 29.40$]

The definite integral on the right may be evaluated by expanding $e^{\beta x^2}$ and integrating term by term. When $N = 82$ (the greatest speed in the potassium iodide experiments), $\beta = 3.484 \times 10^{-4}$ and $A = 0.898\ z_0$; hence when equilibrium is attained at a speed of 82 revolutions per second, the concentration of the iodide at the outer electrode will be 1.213 normal, and at the inner will be 0.904 normal, a ratio of 1.34 to 1.00.

POTASSIUM IODIDE, RATE OF DIFFUSION.

If the motor were stopped after the state of equilibrium had been attained, there would immediately ensue a flow of salt through the solution away from the peripheral end of the tube, the amount of which is given by

$$Concentration\ flow\ towards\ axis = k\frac{\partial z}{\partial x} \quad (4)$$

where k is the diffusion constant (cm^2, sec) of potassium iodide at 20° C. in normal or approximately normal solution. I have taken $k = 14.5 \times 10^{-6}$.

As explained above, this "concentration flow" may be regarded

as just balanced, at equilibrium, by the "centrifugal flow" in the opposite direction; the latter would therefore be represented by

$$\textit{Centrifugal flow toward axis} = -k\frac{\partial z}{\partial x}\textit{at equil.,} = -2k\beta xz \qquad (5)$$

Thus an expression for the centrifugal flow at equilibrium is obtained, and it is assumed that (5) will hold whatever the distribution of concentrations; *i. e.,* that in general

$$\textit{Flow towards axis} = k\frac{\partial z}{\partial x} - 2k\beta xz \qquad (6)$$

When the motor is first started, $\frac{\partial z}{\partial x}$ will be zero, and the "flow" will be negative, *i. e.,* the salt will move towards the outer end of the tube; when equilibrium is attained the flow will be zero; and when the motor is stopped β will be zero, and the flow will become positive in sign, *i. e.,* the salt will move towards the axis.

The *accumulation* at any point of the tube, x cm. from the axis, will then be given by

$$\frac{\partial z}{\partial t} = \frac{\partial}{\partial x}\left(\frac{\partial z}{\partial x} - 2k\beta xz\right) \qquad (7)$$

which is the differential equation sought. It is subject to the conditions that, as no salt can enter or leave the tube, the "flow" at $x=r$ and $x=R$ must be zero, or

$$[\textit{at } x=r \textit{ and } x=R]\ k\frac{\partial z}{\partial x} - 2k\beta xz = 0 \qquad (8)$$

and, moreover, that at the beginning of the experiment the concentration has the uniform value z_0 throughout the tube, *i. e.,*

$$[\textit{at } t = 0]\ z = z_0 \textit{ for all values of } x \textit{ from } r \textit{ to } R \qquad (9)$$

A solution of (7) that will satisfy (8) and (9) will therefore give the concentration at any point of the tube at any moment after rotation has begun.

Such a solution can be arrived at by means of successive approximations; for the present purpose, however, the problem may be simplified by neglecting the very slight variations in the centrifugal flow caused by the slight changes in concentration

which occurred along the tube in Tolman's experiments. Equations (7) and (8) then become.

$$\frac{\partial z}{\partial t} = \frac{\partial}{\partial x}\left(k\frac{\partial z}{\partial x} - 2k\beta x z_0\right) \tag{10}$$

$$[at\ x=r\ and\ x=R]\ k\frac{\partial z}{\partial x} - \beta x z_0 = 0 \tag{11}$$

while equation (9) remains as before.

These three equations, viz., (9), (10) and (11), are satisfied by

$$\frac{z-z_0}{\beta z_0} = \frac{4l^2}{\pi^2}\sum_{n=1}^{\infty}\frac{(-1)^{n+1}}{n^2}\cdot\cos\frac{n\pi(x-r)}{l}\cdot e^{\frac{-n^2\pi^2kt}{l^2}} +$$

$$\frac{8lr}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{(2n-1)^2}\cdot\cos\frac{(2n-1)\pi(x-r)}{l}\cdot e^{\frac{-(2n-1)^2\pi^2kt}{l^2}}$$

$$-\left(r^2 + rl + \frac{l^2}{3}\right) + x^2 \tag{12}*$$

Replacing y by $\pi(x-r)/l$ in the cosine series

$$y^2 = \frac{\pi^2}{3} - 4\sum\frac{(-1)^{n+1}}{n^2}\cos ny$$

$$\text{and } y = \frac{\pi^2}{2} - \frac{4}{\pi}\sum\frac{1}{(2n-1)^2}\cos(2n-1)y$$

(given, for example, in Byerly's "Fourier's Series and Spherical Harmonics," pages 44 and 45), there results

$$x^2 = r^2 + rl + \frac{l^2}{3} - \frac{4l^2}{\pi^2}\sum\frac{(-1)^{n+1}}{n^2}\cos\frac{n\pi(x-r)}{l}$$

$$-\frac{8rl}{\pi^2}\sum\frac{1}{(2n-1)^2}\cdot\cos\frac{(2n-1)\pi(x-r)}{l}$$

whence, for small values of kt/l^2 such as occur in Tolman's experiments,

$$[for\ x = r]\ \frac{z}{z_0} - 1 = -\frac{4R+8r}{3\sqrt{\pi}}\beta\sqrt{kt} \tag{13}$$

$$[for\ x = R]\ \frac{z}{z_0} - 1 = \frac{8R+4r}{3\sqrt{\pi}}\beta\sqrt{kt} \tag{14}$$

*In (12) l is written as a contraction for $R - r$.

In a paper by T. R. Rosebrugh and W. Lash Miller (Jour. Phys. Chem. 14, 826 (1911) equation 21) it is shown that for small values of at

$$\sum_{n=1}^{\infty} \frac{1}{p} e^{-p^2 at} = \frac{\pi^2}{8} - \frac{1}{2}\sqrt{\pi at}, \textit{ approximately}$$

where $p = 2n-1$. From this it may be deducted that when $p = 2n$, the series is approximately equal to $\frac{\pi^2}{24} - \frac{1}{6}\sqrt{\pi at}$.)

As β is proportional to N^2, it follows from (13) and (14) that the time needed to bring about any given small change in concentration at either end of the tube is inversely proportional to the fourth power of the rate of rotation. What is ordinarily considered a rapid centrifuge, running at 2,000 revolutions per minute, would take over half an hour to accomplish what Tolman's apparatus (82 rev. per sec.) did in one minute.

IODINE, CONCENTRATIONS AT EQUILIBRIUM.

In dilute solutions of iodine in normal potassium iodide (where, in the language of the theory of solutions, practically all the free iodine is present as $\overline{I_3}$ or KI_3)

$$[\textit{free iodine}]\ \mu = \textit{const.} + \frac{1.98\theta}{254} \log \textit{nat} \frac{w}{z}$$

where w is the concentration of the iodine (*i. e.*, of the total free iodine determinable by thiosulphate) and z that of the potassium iodide. Introducing this value of μ into equation (1), and neglecting the change of vd with the concentration, there results

$$[\textit{at equil.}]\ \frac{w}{z} = Be^{\gamma x}\ ;\ \textit{where}\ \gamma = 15.18 \times 10^{-8} N^2 \quad (15)$$

[For dilute solutions of iodine in potassium iodide solution Tolman finds $v = 0.2376$; $d = 1.115$ as before.]

Replacing z by its value from (2) gives

$$[\textit{at equil.}]\ w = ABe^{(\beta + \gamma) x^2} \quad (16)$$

in which AB can be determined as A was in (3).

When $N = 82$, $\beta = 3.484 \times 10^{-4}$, $\gamma = 10.21 \times 10^{-4}$, $AB = 0.6345$; thus when equilibrium has been attained at a speed of

82 revolutions per second, the concentration of the free iodine at the outer electrode will be 0.0414 normal ($z_0 = 0.02$ normal), and that at the inner electrode 0.0130 normal, a ratio of 3.18 to 1.00.

IODINE, RATE OF DIFFUSION.

Regarding the flow of free iodine through the solution (towards the axis reckoned positive) as made up of three components, the first of these, that due to differences in iodine concentration, may be set

$$\textit{Iodine-concentration component} = K\frac{\partial w}{\partial x} \qquad (17)$$

[Brunner's experiments (Zeit. phys. Chem. **58** 22-28 (1907)) seem to show that K is about $\frac{2}{3}\,k = 9.7 \times 10^{-6}$; two direct measurements made here by Mr. Pirie, gave 10.4×10^{-6} and 11.6×10^{-6}. In the computations 10×10^{-6} is used.]

where K is the diffusion constant of free iodine in approximately normal potassium iodide. The second, due to centrifugal force, may be set (as in equation 5)

$$\textit{Centrifugal component} = -2K\gamma xw \qquad (18)$$

the third is then determined, since at equilibrium the total flow is zero,

$$\textit{Iodide-concentration component} = 2K\gamma xw - K\frac{\partial w}{\partial x} \textit{ at equil.}$$

$$= -K\frac{w}{z}\frac{\partial z}{\partial x} \qquad (19)$$

The differential equation for the free iodine is therefore

$$\frac{\partial w}{\partial t} = \frac{\partial}{\partial x}\left(K\frac{\partial w}{\partial x} - 2K\gamma xw - K\frac{w}{z}\frac{\partial z}{\partial x}\right) \qquad (20)$$

the boundary and initial conditions being

$$(\textit{at } x = r \textit{ and } x = R)\ \frac{\partial w}{\partial x} - 2\gamma xw - \frac{w}{z}\frac{\partial z}{\partial x} = 0 \qquad (21)$$

$$[\textit{at } t = 0]\ w = w_0 \textit{ for all values of } x \textit{ from } r \textit{ to } R \qquad (22)$$

A solution which fits the conditions of Tolman's experiments

may be obtained by writing z_0 for z in (20) and (21) and replacing $\frac{\partial z}{\partial x}$ by its value from (12), viz., $2\beta z_0 x$. Equation (20) then becomes

$$\frac{\partial w}{\partial t} = \frac{\partial}{\partial x}\left(K\frac{\partial w}{\partial x} - 2K(\beta + \gamma)xw\right) \qquad (23)$$

which is the same in form as (7). Expressions for w at $x=r$ and at $x=R$ valid for small values of Kt/l^2 may therefore be obtained by substituting K for k, w for z, and $\beta+\gamma$ for β in (13) and (14).

ELECTROMOTIVE FORCE OF THE CONCENTRATION CELL.

The net result of passing a current of electricity through the tube, so that the outer electrode is cathode, is that for every 96,540 coulombs 127 grams free iodine are lost at the outer electrode and gained at the inner, and 0.486 × 166 grams* of potassium iodide are gained at the outer and lost at the inner electrode. Writing Z_R, Z_r for the concentrations of the potassium iodide at the outer and inner electrodes respectively, W_R and W_r for those of the free iodine, and assuming that the iodide is 78 percent dissociated, the E.M.F. at 20° C. due to the concentration difference will be

$$E.M.F. = 0.000099 \times 293 \times \log_{10}\frac{W_R Z_r}{W_r Z_R} - 0.000198 \times 293$$

$$\times\ 0.486 \times 1.78 \times \log_{10}\frac{Z_R}{Z_r}\ volts \qquad (24)$$

$$= 0.0126\ \log nat\ \frac{W_R}{W_r} - 0.0344\ \log nat\ \frac{Z_R}{Z_r}\ volts. \qquad (25)$$

When the difference between Z_R and z_0 does not exceed one percent or so, $\log nat\ Z_R$ may be replaced by the right hand member of equation (14), and similarly with the other logarithms; this gives

$$E.M.F. = (R + r)(0.0284\beta + \gamma\sqrt{Kt} - 0.0776\beta\sqrt{kt}) \qquad (26)$$

or, inserting the values of R, r, β, γ, K and k

$$E.M.F. = 1.034 \times 10^{-10} N^2 \sqrt{t}\ volts \qquad (27)$$

*0.486 is the transport number of the cation in potassium iodide solution.

The following table gives the gain or loss at each electrode in percents of the initial concentration, and the resulting E.M.F. in millivolts, for Tolman's three experiments with potassium iodide and iodine; on the assumption that in each case the salt was evenly distributed throughout the solution before rotation began.

N	t Sec.	Iodine		Iodide		E. M. F. Millivolts
		Inner Percent	Outer Percent	Inner Percent	Outer Percent	
62	150	−0.087	+0.144	−0.025	+0.041	0.0049
76	210	−0.154	+0.256	−0.044	+0.074	0.0087
82	60	−0.096	+0.159	−0.028	+0.046	0.0054

After running for fifteen minutes at 82 rev. per sec. there would be a difference of one percent between the concentrations of the iodine at the two electrodes; but even then, owing to the simultaneous changes in concentration of the iodide, the E.M.F. would not reach 0.021 millivolt.

The University of Toronto,
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An Experimental Lecture presented at the Twenty-third General Meeting of the American Electrochemical Society, at Atlantic City, N. J., April 4, 1913, President W. Lash Miller in the Chair.

HYPERBASIS.

LECTURE EXPERIMENTS ON SUPERSATURATION, SUPERCOOLING AND SUPERHEATING.

By Frank B. Kenrick.

The importance of hyperbasis *(Ueberschreitungserschcinungen)* in bringing about thermodynamically "improbable" reactions at the electrodes is now generally recognized, and at the request of the Board of Directors of the Society the illustrated lecture at the present meeting is devoted to this subject. It is hoped that the following notes may make it easy for those who are interested to repeat some of the experiments shown.

APPARATUS.

1. *Projection Cell.* Although lantern cells ("hollow slides") may be obtained commercially, they are often of the wrong shape or size for some special experiment. Moreover, many cells on the market will not stand rapid changes of temperature. The cell described below is free from this objection, and can be easily made or modified in a few minutes.

A glass rod is bent into a U and covered with a rubber tube (*A*, Fig. 1). Near the shorter arm is a second rod, *B*, also covered with rubber tubing. These are clamped, as shown, between two glass plates by means of four strips of wood (1.5 cm. square), *C* and *D*, bolted together at the ends. Hot or cold water, or both, may be led through the tubes, *E* and *F*, the overflow running down between *A* and *B* and being caught in the rectangular tin tray, *G*, on which the lower pair of wooden strips rest and which serves as a stand for the cell. This cell may be made double (see Exp. IV) by clamping, between the same wooden strips, a duplicate cell, in the reverse position, to the right of the cell shown in the diagram. The overflows are thus both on the outside, and do not take up valuable space in the

EXPERIMENTS.

I. Absence of Supersaturation in Solutions of Liquids in Liquids. A good lecture experiment to illustrate this point may be made with a mixture of phenol and water. A flat capillary tube containing water, shaken up with about 20 percent by volume of phenol, is placed alongside the projection thermometer in the lantern cell. When the temperature is gradually raised and lowered the tube becomes suddenly transparent and opaque alternately, at practically the same temperature, as the saturation point is passed. The capillary tube should be about 3 mm. wide by 0.5 mm. thick, inside dimensions. Such tubes may be made by flattening a bulb with a pair of tongs, reheating, and pulling out.

The difficulty of obtaining supersaturated solutions of liquids in liquids has been noted by several observers (Rothmund,[1] Füchtbauer,[2] Fawcett[3]). Füchtbauer suggests that dust particles, which are probably amorphous, act as nuclei for liquids and not for crystalline substances. He himself, however, observed that purification of the liquid made very little, if any, difference. Fawcett obtained similar results. It is possible that the cause of the small degree of supersaturation of liquids is connected with the comparatively small surface tension of the interface between liquid and liquid. At any rate, the following calculations in two typical cases, for which data are available, are of interest. Taking the surface energy of the interface gypsum-saturated solution as 550 ergs per sq. cm.,[4] and assuming arbitrarily the radius of the particles initially formed to be 15 $\mu\mu$ (0.0000015 cm.),[5] a simple calculation shows that, for equilibrium, the solution would have to be about six times as strong as the normally saturated solution. This is probably well beyond the limit of supersaturation actually relizable. On the other hand, in the case of isobutyric acid and water, the surface energy of whose interface is 1.76 ergs, particles of the acid with a radius

[1] Zeit. phys. Chem., 26, 444 (1898).

[2] Zeit. phys. Chem., 48, 566 (1904).

[3] Proc. Roy. Soc. Canada, 1913.

[4] Hulett, Zeit. phys. Chem., 37, 404 (1901). A slip in the calculation of this value was corrected by Freundlich, "Capillarchemie," 1909, p. 144, but Freundlich takes Hulett's value for the diameter of the particles instead of the radius. With this additional correction the value is 550.

[5] 15 $\mu\mu$ is the thickness of the black spot in a soap bubble. This value is also within the limits of the various experimentally determined thicknesses of films of matter which show the properties of the substances in mass.

of 15 $\mu\mu$ would be in equilibrium with a solution only 0.8 percent stronger than the normally saturated solution. At the ordinary temperature this corresponds to a change of temperature of about 0.5°.[6] Since it is very difficult to determine accurately the temperatures at which turbidity appears and disappears—the identity of which is the usual criterion for absence of supersaturation—a difference of this order of magnitude might easily escape observation.

II. Superheating of Liquids. It is very easy to superheat liquids in small, clean tubes. When a liquid begins to boil, the ebullition usually takes place quite locally, either at a few fixed points on the walls of the vessel or from particles suspended in the liquid from which streams of bubbles may be seen rising. The smaller the vessel and the smaller the volume of the liquid the less is the chance of the presence of these starting-points for bubbles. It appears, moreover, that there is a gradation in the effectiveness of the nuclei present—*i. e.*, some will cause ebullition when the liquid is slightly superheated, while others will not become effective until the liquid is heated to a higher temperature—for the smaller the tube the higher is the temperature to which the liquid can be heated without boiling. This is in accordance with the law of probability; the nuclei of medium effectiveness are the most abundant, and therefore, on decreasing the size of the tube, the most (and least) effective nuclei are the first to disappear. This may be shown in the projection cell by gradually heating simultaneously three glass tubes (0.7 mm., 1.5 mm. and 3 mm. internal diameter) half filled with ether. The largest tube may be heated to about 60°, when suddenly either all or part of the ether jumps out of the tube. In the second tube the ether does not explode until the temperature has risen many degrees higher, while the smallest tube may often be heated to over 90° without the hyperbasis being relieved, although the ether may be seen to be evaporating with great rapidity at the free surface.

The effect of the insertion of a fine capillary tube, open at the lower end, may be shown in the larger tube of ether, superheated to about 50°. Also the effect of a grain of pipe clay and of a platinum wire may be demonstrated in the same tube. The latter

[6] Alexjew, Wied. Ann. 28, 305 (1886).

causes a temporary disturbance, but generally loses its effectiveness after a few seconds.

It is interesting to note that, if the same assumption be made as in the previous experiment as to the initial size of the bubbles (15 $\mu\mu$), and if the surface energy of ether at 90° is taken as 9 ergs,[7] a calculation of the pressure in the bubbles gives a value of about 12.5 atmospheres. This corresponds to a temperature of about 130° (extrapolated).

III. Linear Rate of Crystallisation. The relation between temperature and linear rate of crystallisation may be shown with melted vanillin. A thin-walled capillary tube about 1 mm. in diameter containing solidified vanillin is immersed in the projection cell to within about 3 cm. of the bottom, and boiling water run through the cell. This melts all the vanillin below the surface of the water, but leaves a quantity of unmelted solid in the upper end of the tube. The water is then cooled to about 75°, and the tube pushed down further into the cell and held in position against the thermometer scale with a cork wedge. At the same time the second pendulum described in paragraph 4 is set in motion. The rate of crystallisation is measured by the number of marks on the thermometer traversed by the edge of the solid during 20 seconds. The temperature of the cell is lowered by about 5° at a time, and successive readings of rate and temperature are taken as the crystallisation proceeds. If the lantern has a vertical attachment the relation between rate and temperature may be plotted on smoked glass and shown on the screen after each measurement. By timing the intervals properly, a complete curve showing the initial increase in rate below the melting point, the interval of constant rate, and the final decrease in rate with falling temperature, may be plotted on the glass before the crystallisation has reached the end of the tube. The measurements cannot be made below about 37°, since spontaneous crystallisation from nuclei begins at this temperature.

IV. Nuclei and Crystallisation. The relation between the number of nuclei and the temperature and duration of supercooling may be shown by Tammann's "exposure and development" method.[8] A double projecting cell is used, each section

[7] Ramsay and Shields, Zeit. phys. Chem., **12**, 442 (1893).
[8] Zeit. phys. Chem., **25**, 441 (1898).

of which may be heated and cooled rapidly. Vanillin (MP = 81°) is the most satisfactory substance to use for these experiments. A flattened capillary tube, about 2 mm. x 0.5 mm. inside dimensions, is filled with vanillin, melted in one side of the cell in boiling water, quickly transferred to the other half of the cell, at (say) 20°, and "exposed" for a definite number of seconds (say 5), as shown by the shadow of the pendulum, and finally put back quickly into the first cell, which in the meantime has been cooled to a suitable "development" temperature (60°). It is easier to count the nuclei if the tube is put back into the cold half of the cell immediately they begin to appear; this checks the otherwise too rapid growth. The temperature and time of exposure may, of course, be varied.

For these experiments it is convenient to arrange the four tubes conducting hot and cold water to the two halves of the cell so that they pass through four spring pinch-cocks, fixed in a row on a board. By this means the temperatures of the two parts of the cell may be controlled by the four fingers of one hand, thus leaving the other hand free to manipulate the capillary tube.

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